On the application of an approximate kinetic equation of heat and mass transfer processes: the effect of body shape

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Abstract An approximate kinetic equation of heat and mass transfer has been presented. It is an ordinary differential equation which is easy to integrate. The derivation of this approximation was based on an analysis of the available analytical solution of the problem. The proposed equation can be applied to bodies (pellets) in the shape of an infinite slab, infinite cylinder and sphere. A generalization of this equation to cases where the transfer resistance occurs both in the body and in the surrounding fluid has been proposed. The equation has been tested in various conditions both for thermal and diffusive processes. Radiative cooling of bodies has been considered as a thermal process and adsorption in a single pellet—as a diffusive process. All tests showed high accuracy of the approximate equation; in many cases the results were indistinguishable from the results of the exact model. A special feature of the proposed equation is its high accuracy for short times of the process, what significantly differentiates it from the classical approximate kinetic equation Linear Driving Force.

List of symbols

$\bar{A}, A$	Dimensionless temperatures or concentrations defined by Eqs. 8 and 9
b	Geometric factor
Bi	Mass Biot number
c_p	Specific heat of body, J kg ⁻¹ K ⁻¹

c_1, c_2, c_3	Coefficients of polynomial
C	Concentration of mixture component, kg/m ³
D_s	Diffusion coefficient, m ² s ⁻¹
F	Defined by Eq. 40
$J_0(a)$	Bessel function of the first kind of order 0
k	Thermal conductivity of body, W m ⁻¹ K ⁻¹
k_g	Mass transfer coefficient, m s ⁻¹
k_h	Defined by Eq. 31
K	Defined by Eq. 32
N_{rc}	Radiation–conduction parameter (Eq. 45)
q_m	Solid phase concentration, kg component/kg solid
R_p	Radius of pellet, m
s	Characteristic geometric dimension of body, m
T	Temperature, K
t	Time, s
x	Spatial coordinate, m
y_{mol}	Mole fraction of mixture component
Y	Dimensionless concentration in gas phase

Greek symbols

$\alpha(=k/(c_p\rho))$	Thermal diffusivity, m ² s ⁻¹
β_n	Defined by Eq. 26a
ε	Surface emissivity
η	Dimensionless spatial coordinate (Eq. 11)
σ	Stefan–Boltzmann constant (=5.67 × 10 ⁻⁸ W m ⁻² K ⁻⁴)
τ	Dimensionless time (Eq. 12, Table 2)
ρ	Density, kg m ⁻³

Subscripts and superscripts

b	Bulk
ex	Exact
i	Initial
0	Body center

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- 1 Body surface
 – Average value

1 Introduction

In modeling of thermal or diffusion processes occurring under transient conditions the balance of heat or mass within the body is often taken into account. As a result a spatial coordinate occurs in equations of the model. Approximate kinetic equations are used to avoid it. For example, the model of radiative cooling of the body is based on the equation of transient heat conduction with the boundary condition for the surface in the form of the Stefan-Boltzmann equation of heat radiation. A key difficulty in solving equations of this model is that we are dealing with a partial differential equation with a nonlinear boundary condition. Numerical solution of this problem is time consuming. This is particularly important when calculations are performed repeatedly within a complex procedure. Such a problem appears e.g. in computational fluid dynamics (CFD). Therefore, it is advantageous to adopt a simplification which results in elimination of the spatial coordinate in the body. Then the process will be described with an ordinary differential equation. Similarly, in modeling of adsorption processes one has to determine the rate of mass transfer between the surface of the adsorbent pellets and the fluid. In this case, the concentration of adsorbed component on the surface of a pellet and the average concentration of the component in the pellet are important. Approximate equations of adsorption kinetics determine the rate of mass transfer (adsorption) as a function of the difference between the concentration on the pellet surface and the average concentration (considered as a driving force of the process), whereas the concentration profile of the component in the body is generally unnecessary. The most widely used approximate kinetic equation is the Glueckauf equation (LDF) [1] utilized in modeling and design of adsorption processes:

$$\frac{d\bar{q}_m}{dt} = k_{LDF}(q_{m1} - \bar{q}_m) \quad (1)$$

where $k_{LDF} = \text{const}$. This equation is often used, despite the fact that it is inaccurate to the initial stage of the process (i.e., for short time).

The LDF equation can be derived on the basis of the assumption of parabolic profile of component concentration in an adsorbent pellet [2, 3]. This equation is also utilized in thermal processes modeling [4, 5]. In the last paper the LDF equation was used in a model describing radiative cooling.

A new approximate kinetic equation, valid for both long and short durations of the process of transient heat or mass transfer has recently shown [6]. This equation was developed for a spherical body and applied in the modeling of a

radiative cooling process. The results of the model based on this equation were compared with the exact numerical solution. Very good agreement between the approximate and exact results was obtained. It is worth noting that satisfactory agreement relates to all bodies, irrespective of their ability to conduct heat.

In this paper a generalization of the approximate kinetic equation for a sphere shown in [6] is developed for other simple shapes (slab, cylinder). Approximate generalized equation was tested numerically for various cases of heat and mass transfer:

- The temporal variations of temperature during radiative cooling of the bodies in the shape of a slab and cylinder, obtained on the basis of two models: a model based on the approximate kinetic equation and the exact model, are compared.
- The values of diffusion coefficient in the adsorbent pellets were determined on the basis of measurements of adsorption kinetics. Calculations were based on the approximate kinetic equation and the exact equation of diffusion. Comparisons were made for two series of measurement:
 - (a) Results of own measurements (spherical pellets),
 - (b) Results of measurements taken from literature (pellets in the shape of a slab).

Utilization of approximate kinetic equations greatly simplifies modeling of thermal and diffusion processes, while only slightly lowers accuracy of calculations. Considering the field of thermal processes, approximate equations may be used in problems related to heating or cooling of solids. Such problems were considered i.a. in works [7] and [8]. Approximate kinetic equations have been used in mass transfer processes for many years, especially in modeling of adsorption processes [3]. A method for using approximate kinetic equations is presented in Chaps. 4 and 5.

2 General relationships

Heat conduction is described by the following equation:

$$\frac{\partial T}{\partial t} = \frac{\alpha}{x^{b-1}} \frac{\partial}{\partial x} \left(x^{b-1} \frac{\partial T}{\partial x} \right) \quad (2)$$

where b is a geometric factor, different for each shape (Table 1). The following initial condition will be taken under consideration:

$$T = T_i \quad \text{for } t = 0 \quad (3)$$

One of the boundary conditions results from the symmetry of the body:

$$\frac{\partial T}{\partial x} = 0 \quad \text{for } x = 0 \quad (4)$$

Table 1 Relations and values for particular shapes

Shape	b	V_{body}	A_x	A_{body}	s	β_1
Slab (infinite)	1	$2A_{sl}s$	$2A_{sl}$	$2A_{sl}$	Half of thickness	1.5708
Cylinder (infinite)	2	$\pi s^2 L$	$2\pi xL$	$2\pi sL$	Radius	2.4048
Sphere	3	$4/3 \cdot \pi s^3$	$4\pi x^2$	$4\pi s^2$	Radius	3.1416

A_{sl} surface area of one side of slab, L length of cylinder

Table 2 Overview of quantities and equation for processes of heat and mass transfer

Quantity or equation	Heat transfer	Mass transfer
$\bar{A}$	$\frac{T_i - \bar{T}}{T_i - T_b}$	$\frac{q_{mi} - \bar{q}_m}{q_{mi} - q_{mb}}$
A	$\frac{T_i - T}{T_i - T_b}$	$\frac{q_{mi} - q_m}{q_{mi} - q_{mb}}$
τ	$\alpha t / s^2$	$D_s t / s^2$
Eqs. 2–7	T	q_m
Eq. 2	α	D_s
$\frac{Q_t}{A_{\text{body}}}$ Eq. 18	$\frac{2}{\sqrt{\pi}} (T_i - T_b) \rho c_p \sqrt{\alpha t}$	$\frac{2}{\sqrt{\pi}} \rho (q_{mi} - q_{mb}) \sqrt{D_s t}$

The second boundary condition on a body surface depends on the case under consideration. Firstly, let us consider the condition related to the constant temperature of the body surface (Dirichlet condition):

$$T_1 = T_b \quad \text{for } x = s \quad (5)$$

An average body temperature can be determined on the base of the following balance equation (T_{ref} any reference temperature):

$$V_{\text{body}} (\bar{T} - T_{ref}) = \int_0^s A_x (T - T_{ref}) dx \quad (6)$$

The value of volume of a body of any shape V_{body} , external surface area A_{body} , surface area perpendicular to the direction of heat transport A_x , and characteristic geometric dimension s are shown in Table 1. After integration of Eq. 6 one can obtain a relation to calculate an average temperature:

$$\bar{T} = \frac{b}{s^b} \int_0^s x^{b-1} T dx \quad (7)$$

For a body of mass m_{body} the amount of heat Q_t lost from the beginning of the process to the given moment is proportional to $T_i - \bar{T}$, whereas the total amount of heat Q_{∞} , which is lost from the beginning of the process to the time in which the thermal equilibrium is reached, is

proportional to $T_i - T_b$. A dimensionless temperature $\bar{A}$, characterizing a ratio of the heat amount emitted by a body from process beginning to the total heat amount available for emission ($=Q_t/Q_{\infty}$), has been defined:

$$\bar{A} = \frac{T_i - \bar{T}}{T_i - T_b} \quad (8)$$

Analogically, a local dimensionless temperature A characterizing a ratio of the local heat amount emitted out to the total heat amount available for emission has been defined:

$$A = \frac{T_i - T}{T_i - T_b} \quad (9)$$

For mass transfer processes, quantities resulting from the analogy between heat and mass transfer occur in these relations. They are summarized in Table 2. The following relation between A and $\bar{A}$ can be easily obtained:

$$\bar{A} = b \int_0^1 \eta^{b-1} A d\eta \quad (10)$$

where η is a dimensionless spatial coordinate:

$$\eta = \frac{x}{s} \quad (11)$$

When introducing the dimensionless spatial coordinate η and the dimensionless time τ (Table 2):

$$\tau = \frac{\alpha t}{s^2} \quad (12)$$

the equation of heat conduction (or diffusion) can be converted into the form:

$$\frac{\partial A}{\partial \tau} = \frac{1}{\eta^{b-1}} \frac{\partial}{\partial \eta} \left(\eta^{b-1} \frac{\partial A}{\partial \eta} \right) \quad (13)$$

with initial condition:

$$A = 0 \quad \text{for } \tau = 0 \quad (14)$$

and boundary conditions:

$$\frac{\partial A}{\partial \eta} = 0 \quad \text{for } \eta = 0 \quad (15)$$

$$A_1 = 1 \quad \text{for } \eta = 1 \quad (16)$$

When differentiating Eq. 10 towards time and taking into account the differential Eq. 13 one can get:

$$\frac{d\bar{A}}{d\tau} = b \left(\frac{\partial A}{\partial \eta} \right)_1 \quad (17)$$

For short process times the shape of the body is irrelevant; on the basis of the theory of penetration one can conclude

that in this case the amount of heat related to the external body surface is [9]:

$$\frac{Q_t}{A_{\text{body}}} = \frac{2}{\sqrt{\pi}} (T_i - T_b) \rho c_p \sqrt{\alpha t} \quad (18)$$

Mass transfer Eq. 18 has the form resulting from Table 2. This equation is independent of the body shape, as one would expect for short time the heat (mass) penetration is still very close to the exterior surface and the body curvature is irrelevant. The heat (mass) transfer is only controlled by the available external surface area. Since $\bar{A} = Q_t/Q_\infty$, thus:

$$\bar{A} = \frac{2}{\sqrt{\pi}} \frac{A_{\text{body}}}{V_{\text{body}}} \sqrt{\alpha t} \quad (19)$$

For a body of any shape the ratio of external surface to its volume is:

$$\frac{A_{\text{body}}}{V_{\text{body}}} = \frac{b}{s} \quad (20)$$

Hence, for any body shape the following relation is valid for short times:

$$\bar{A} = 2b \sqrt{\frac{\tau}{\pi}} \quad (21)$$

Crank [10] gives more complex relations for short times. For a cylinder and sphere these equations take into account a curvature of a body surface, which is not taken into consideration in relations of type Eq. 21. For an infinite slab:

$$\bar{A} = 2\sqrt{\tau} \left(\sqrt{\frac{1}{\pi}} + 2 \sum_{n=1}^{\infty} (-1)^n \text{ierfc} \frac{n}{\sqrt{\tau}} \right) \quad (22)$$

For an infinitely long cylinder:

$$\bar{A} = \frac{4}{\sqrt{\pi}} \sqrt{\tau} - \tau - \frac{1}{3\sqrt{\pi}} \tau^{3/2} + \dots \quad (23)$$

For a sphere:

$$\bar{A} = 6\sqrt{\tau} \left(\sqrt{\frac{1}{\pi}} + 2 \sum_{n=1}^{\infty} \text{ierfc} \frac{n}{\sqrt{\tau}} \right) - 3\tau \quad (24)$$

Terms of above equations containing a function ierfc extend the applicability of these models beyond the short times. Thus, they can be omitted for short times. For a sphere and short times the following equation is often utilized:

$$\bar{A} = 6\sqrt{\frac{\tau}{\pi}} - 3\tau \quad (25)$$

Analytical solutions for different shapes are presented in works of Crank [10] and Carslow and Jaeger [11]. An

analytical solution of Eq. 13 with conditions Eqs. 14–16, generalized for different shapes, has the following form:

$$\bar{A} = 1 - 2b \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp(-\beta_n^2 \tau) \quad (26)$$

$$\text{where: } \begin{aligned} \beta_n &= (2n-1) \cdot \pi/2 && \text{for slab,} \\ \beta_n &= n\text{th non-zero root of } J_0(\alpha) = 0 && \text{for cylinder,} \\ \beta_n &= n\pi && \text{for sphere.} \end{aligned} \quad (26a)$$

Values of β_1 for considered shapes are presented in the last column of Table 1.

Relations between $\bar{A}$ and dimensionless time τ are presented in Fig. 1a, b and c for each shape: an infinite slab, infinite cylinder, and sphere. These figures also display temporal variations of $\bar{A}$ resulting from the use of different forms of formulas Eqs. 22–24 valid for short process times. In addition, the variation of $\bar{A}$ versus τ resulting from the equation valid for long times is depicted. In the latter case the series in Eq. 26 is quick-convergent and only the first summand is important. Thus, for $\tau \rightarrow \infty$:

$$\bar{A} = 1 - \frac{2b}{\beta_1^2} \exp(-\beta_1^2 \tau) \quad (27)$$

On the base of Fig. 1a, b and c it can be concluded that the ranges in which equations for short times give results consistent with the exact solution are quite wide and different for different shapes.

3 Approximate kinetic equation

The temporal derivative of $\bar{A}$ is given by differentiation of Eq. 26:

$$\frac{d\bar{A}}{d\tau} = 2b \sum_{n=1}^{\infty} \exp(-\beta_n^2 \tau) \quad (28)$$

Differentiation of Eq. 27, which relates to long times, leads to:

$$\frac{d\bar{A}}{d\tau} = 2b \cdot \exp(-\beta_1^2 \tau) = \beta_1^2 (1 - \bar{A}) \quad (29)$$

For short times ($\bar{A} \rightarrow 0$) the time derivative was determined from Eq. 21:

$$\frac{d\bar{A}}{d\tau} = \frac{b}{\sqrt{\pi\tau}} = \frac{2b^2}{\pi\bar{A}} \quad (30)$$

In this paper an approximate kinetic equation has been employed. This equation is based on the following functions:

$$k_h = \frac{d\bar{A}/d\tau}{1 - \bar{A}} \quad (31)$$

Fig. 1 **a** Dependence between $\bar{A}$ and τ for slab, **b** dependence between $\bar{A}$ and τ for cylinder, **c** dependence between $\bar{A}$ and τ for sphere

and

$$K = (k_h - \beta_1^2) \cdot \bar{A} \quad (32)$$

The expression $k_h = (d\bar{A}/d\tau)/(1 - \bar{A})$ acts as the heat (mass) transfer coefficient [12]. In accordance to Eq. 29 for $\bar{A} \rightarrow 1$ (long times) the implication $k_h = \beta_1^2$ occurs as well as

$$\lim_{\bar{A} \rightarrow 1} K = 0 \quad (33)$$

It results from Eqs. 30, 31 and 32 that for small values of $\bar{A}$:

$$K = \frac{2b^2}{\pi(1 - \bar{A})} - \beta_1^2 \bar{A} \quad (34)$$

So:

$$K_0 = \lim_{\bar{A} \rightarrow 0} K = \frac{2b^2}{\pi} \quad (35)$$

Graphical interpretation of the relationship between K and $\bar{A}$ is shown in Fig. 2. To enable comparison of variation of the function for each body shape, quantity K was normalized to the interval (0,1) by dividing by K_0 . Then for $\bar{A} = 0$ is $K/K_0 = 1$ for each shape. According to Eq. 35 values of K_0 are as follows: for slab $K_0 = 2/\pi$, for cylinder $K_0 = 8/\pi$, for sphere $K_0 = 18/\pi$. Variations in Fig. 2 corresponds with analytical solution of the equation of heat conduction/diffusion in a slab, cylinder and sphere with the boundary condition of Dirichlet type Eq. 5.

The approximate equation has been based on K versus $\bar{A}$ function approximation with a third degree polynomial:

$$K \cong c_0 + c_1(1 - \bar{A}) + c_2(1 - \bar{A})^2 + c_3(1 - \bar{A})^3 \quad (36)$$

The relations Eqs. 33 and 36 give $c_0 = 0$ while relations Eqs. 35 and 36 lead to the result:

Fig. 2 Exact variations of relationship between K/K_0 and $\bar{A}$ for considered body shapes

$$c_1 + c_2 + c_3 = \frac{2b^2}{\pi} \quad (37)$$

Equation 36 can be written in the form:

$$K = \left(\frac{2b^2}{\pi} - c_2 - c_3 \right) (1 - \bar{A}) + c_2 (1 - \bar{A})^2 + c_3 (1 - \bar{A})^3 \quad (38)$$

After transformations one can obtain:

$$F = c_3 \bar{A} - (c_2 + 2c_3) = a_1 \bar{A} + a_0 \quad (39)$$

where

$$F = \frac{1}{\bar{A}} \left(\frac{K}{1 - \bar{A}} - \frac{2b^2}{\pi} \right) \quad (40)$$

Variation of F versus $\bar{A}$, resulting from the exact solution of Eq. 13 with conditions Eqs. 14–16, is depicted in Fig. 3 in the form of symbols. This variation has been approximated using a linear function (relation Eq. 39, solid lines in Fig. 3). The found coefficients a_1 and a_0 and the resulting coefficients c_1 , c_2 , c_3 of the polynomial Eq. 36 for each body shape are shown in Table 3.

The variation of K versus $\bar{A}$, resulting from the polynomial approximation, is depicted in Fig. 4 in the form of a solid line. As can be seen, the run of approximating function coincides with the exact one (symbols). The approximate kinetic equation has been obtained by comparison of right sides of Eqs. 32 and 36. It has the form:

Fig. 3 Approximation of relation between F and $\bar{A}$ for considered body shapes

Table 3 Coefficients of the polynomial Eq. 36

Shape	$c_2 + 2c_3 (= -a_0)$	c_0	c_1	c_2	$c_3 (= a_1)$
Slab	1.4627	0	-0.0523	-0.0849	0.7738
Cylinder	2.5270	0	-0.5449	3.6558	-0.5644
Sphere	2.8850	0	-0.3259	9.2260	-3.1705

Fig. 4 Comparison of exact and approximate relations between K and $\bar{A}$

$$\frac{d\bar{A}}{d\tau} = \left[\beta_1^2 + \frac{1}{\bar{A}} \sum_{j=1}^3 c_j (1 - \bar{A})^j \right] \cdot (1 - \bar{A}) \quad (41)$$

The approximate kinetic Eq. 41 refers to the boundary condition Eq. 16, i.e. time-invariant value of A_1 on the surface of the body. Condition Eq. 16 means the absence of transfer resistance outside the body. For cases where resistance is present ($A_1 < 1$) a generalization of Eq. 41 was proposed. The generalized equation has the form [6]:

$$\frac{d\bar{A}}{d\tau} = \left[\beta_1^2 + \frac{1}{A_1 \bar{A}} \sum_{j=1}^3 c_j A_1^{2-j} (A_1 - \bar{A})^j \right] \cdot (A_1 - \bar{A}) \quad (41a)$$

For $A_1 = 1$, Eq. 41a has the form Eq. 41.

One of frequently used approximate kinetic equations is the LDF equation [1–6, 12]. This equation can be derived assuming a parabolic profile of A in the body. Derivation for solids of any shape is presented in “Appendix”. Combining the obtained relationship Eq. 66 with a formula Eq. 17, one can obtain:

$$\frac{d\bar{A}}{d\tau} = b(b+2) \cdot (A_1 - \bar{A}) \quad (42)$$

The dimensional form of this equation was discussed in relation to mass transfer processes in the introduction Eq. 1.

For a numerical solution of kinetic Eqs. 41a or 42 the value of A_1 at each time step of calculations is necessary because this value varies during the process. A_1 is calculated by solving an algebraic equation resulting from comparison of right sides of respective kinetic Eqs. 41a or 42 with relation Eq. 17.

For cases where the transfer resistance in the body is small, the kinetics of heat or mass transfer processes can be described by a lumped model, which is based on the assumption that the dimensionless temperature (concentration) A is invariable in the whole volume of the body.

4 Radiative cooling

In some cases, e.g. in outer space technologies as well as in cryogenic engineering, the surface transmitting the heat is surrounded with vacuum. Therefore, the mechanism of heat convection does not exist and radiation is the only heat transfer mechanism between the body surface and the environment. In this chapter the cooling of body has been considered in the described case.

From body surface the heat is transported to the environment by radiation. Hence, the following boundary condition for surface arises [5, 13, 14]:

$$-k \left(\frac{\partial T}{\partial x} \right)_1 = \varepsilon \sigma (T_1^4 - T_b^4) \quad \text{for } x = s \quad (43)$$

Radiative cooling is usually considered for the case where $T_b = 0$ [5, 15]. In this case the dimensionless form of a condition Eq. 43 can be written as follows:

$$\left(\frac{\partial A}{\partial \eta} \right)_1 = N_{rc} (1 - A_1)^4 \quad \text{for } \eta = 1 \quad (44)$$

where:

$$N_{rc} = \frac{\varepsilon \sigma s T_i^3}{k}. \quad (45)$$

The N_{rc} parameter characterizes the ratio of heat conduction resistance to heat radiation resistance. When the heat conduction resistance equals zero ($k \rightarrow \infty$), then $N_{rc} = 0$. In such case the rate of body cooling is controlled only by heat radiation resistance. Contrary, when the heat radiation resistance equals zero, then $N_{rc} \rightarrow \infty$, and the rate of body cooling is controlled only by heat conduction resistance.

Substituting condition Eq. 44 into Eq. 17, one can obtain:

$$\frac{d\bar{A}}{d\tau} = b N_{rc} (1 - A_1)^4 \quad (46)$$

The approximate kinetic Eq. 41a was tested by applying it for modeling of radiative cooling process for various values of radiation-conduction parameter N_{rc} . Variations of $\bar{A}$ versus τ were determined using an exact model (distributed model) based on Eq. 13 with boundary conditions Eqs. 14–16 and a model based on the approximate equation. The variations of relation between $\bar{A}$ and τ for both the LDF model and the classical lumped model have also been determined for comparison. Error δ have been employed as a measure of deviations between the numerical values obtained from the approximate (*app*) and distributed models (*ex*). It has been defined as follows:

$$\delta = \frac{(1 - \bar{A})_{app} - (1 - \bar{A})_{ex}}{(1 - \bar{A})_{ex}}. \quad (47)$$

The following models have been considered:

Distributed (exact) model. For exact solution of Eq. 13 with initial condition Eq. 14 and mixed boundary conditions Eqs. 15, 16 a procedure based on Crank-Nicolson scheme [16] has been employed. To obtain $\bar{A}$ value it was necessary to apply the integration in accordance with relation Eq. 10. The Simpson method has been employed. The values of function have been calculated using the Lagrange interpolative formula.

Simplified model proposed in this work. Equation 41a has been integrated numerically using the Runge-Kutta method. Values of A_1 have been calculated numerically from following algebraic equation using the Newton method

$$\left[\beta_1^2 + \frac{1}{A_1 \bar{A}} \sum_{j=1}^3 c_j A_1^{2-j} (A_1 - \bar{A})^j \right] \cdot (A_1 - \bar{A}) = b N_{rc} (1 - A_1)^4 \quad (48)$$

The above equation results from comparison of right sides of relations Eqs. 41a and 46. If A_1 is determined, one can integrate numerically the ordinary differential Eq. 41a.

LDF model. Equation 42 has been integrated numerically using the Runge–Kutta method. Values of A_1 have been calculated numerically from following algebraic equation using the Newton method.

$$N_{rc}(1 - A_1)^4 = (b + 2)(A_1 - \bar{A}) \quad (49)$$

This equation is a result of comparison of right sides of Eqs. 42 and 46.

Classical lumped model. For lumped model $A_1 = \bar{A}$; therefore:

$$\frac{d\bar{A}}{d\tau} = b N_{rc} (1 - \bar{A})^4 \quad (50)$$

Integrating this equation with initial condition $\bar{A} = 0$ for $\tau = 0$, one can obtain the analytical solution in the form:

$$\bar{A} = 1 - (1 + 3b N_{rc} \tau)^{-1/3} \quad (51)$$

Figure 5a and b show temporal variations of $\bar{A}$ values predicted by both the distributed model and the presented approximate model for various values of radiation-conduction parameter N_{rc} . Figure 5a refers to the body in the shape of an infinite slab, and Fig. 5b refers to an infinite cylinder. The higher value of radiation-conduction

parameter, the greater is the value of $\bar{A}$ for a given time. For the extreme case when $N_{rc} \rightarrow \infty$ the exact run has been determined on the base of Eq. 26. Moreover, it can be observed that the approximate and exact values are very close in the whole range of N_{rc} values. Therefore, the proposed simplified model is not limited in employment only to good heat conductors. The model predicts accurate results in extreme cases: for very small and very large ($N_{rc} \rightarrow \infty$) values of radiation-conduction parameter. Variation of the function for the body in the shape of a sphere is presented in [6].

Figure 6a, b and c present relations between relative error δ defined by Eq. 47 and the dimensionless time for $N_{rc} = 8$. Charts concern a slab, cylinder, and sphere, respectively. In addition to a course corresponding to the equation considered in this work, courses for LDF and classical lumped models are also presented. Maximum error of the approximate model presented in this work is equal to 2.2% for slab, 3.2% for cylinder, and 3.7% for sphere. The LDF model gives bigger but still permissible maximum errors. Errors of classical lumped model are unacceptable.

Table 4 gives the maximum deviations defined by Eq. 47 for particular models, particular shapes and various values of N_{rc} parameter.

5 Mass transfer in adsorbent pellet

In order to verify the kinetic relation Eq. 41a for mass transfer processes, the results of kinetic measurements

Fig. 5 a Temporal variation of $\bar{A}$ for various N_{rc} for slab, b temporal variation of $\bar{A}$ for various N_{rc} for cylinder

Fig. 6 **a** Temporal variation of δ at $N_{rc} = 8$ for various models for slab, **b** Temporal variation of δ at $N_{rc} = 8$ for various models for cylinder, **c** Temporal variation of δ at $N_{rc} = 8$ for various models for sphere

Table 4 Maximum values of δ for various models and shapes

N_{rc}	$\delta_{\max}, \%$								
	Classical lumped model			LDF model			Proposed model		
	Slab	Cylinder	Sphere	Slab	Cylinder	Sphere	Slab	Cylinder	Sphere
0.7	-8.2	-6.5	-5.4	0.8	0.8	0.7	1.1	1.4	1.6
1.5	-13.9	-11.4	-9.6	1.5	1.6	1.6	1.4	2.0	2.3
3.5	-22.5	-19.0	-16.5	2.6	3.1	3.1	1.9	2.7	3.0
8.0	-32.4	-28.1	-25.0	4.0	4.9	5.2	2.2	3.2	3.7
20	-43.8	-39.2	-35.7	5.5	7.1	7.7	2.5	3.8	4.4
200	-68.0	-64.5	-	9.0	12.4	14.0	3.0	4.5	4.6

presented in the literature [17, 18] were utilized. Using the approximate Eqs. 41 or 41a and having these results, one designated values of diffusion coefficient in adsorbent pellet with different shapes. Both the case of diffusion resistance in the pellet and a combination of internal and external diffusion resistances were considered. Systems in which the dominant mass transfer resistance in a pellet is diffusion in micropores were analyzed.

The calculations were carried out as follows. The value of the effective diffusion coefficient D_s was assumed and the value of a time constant of diffusion was determined:

$$t_D = \frac{s^2}{D_s} \quad (52)$$

Then dimensionless times τ_i were attributed to individual values of times when the measurements were conducted (t_i , $i = 1, 2, \dots, n$)

$$\tau_i = \frac{t_i}{t_D}. \quad (53)$$

Using the appropriate algorithm of calculations (discussed further), one designated values of $\bar{A}$ for individual values of τ . Finally, in order to match the values of calculations (*calc*) to experimental values (*exp*), the sum of squared deviations was created

$$S = \sum_{i=1}^n (\bar{A}_{i,\text{exp}} - \bar{A}_{i,\text{calc}})^2 \quad (54)$$

The sum had to be minimized. The value of a diffusion coefficient for which $S = \min$ was assumed to be the correct one.

At the beginning of considered processes there was no adsorptive component in the pellet ($q_{mi} = 0$); thus according to Table 2

$$\bar{A} = \frac{\bar{q}_m}{q_{mb}} \quad (55)$$

where q_{mb} is the equilibrium content of a component in the pellet in relation to its mole fraction in the bulk of the gas phase y_{molb} .

5.1 Adsorption of cyclohexane on silicalite

In the work of Cavalcante and Ruthven [17] authors consider the process in which plate-like adsorbent pellets with crystal dimensions of $66 \times 66 \times 223 \mu\text{m}$ were adsorbing cyclohexane at temperature of 300°C . Partial pressure of cyclohexane vapor was 2,260 Pa. The results of measurements are presented in Fig. 7 in the form of symbols.

Determination of the value of $\bar{A}$ corresponding to dimensionless time τ using the exact method was based on numerical solution of a partial differential Eq. 13 for $b = 1$ with conditions Eqs. 14–16. However, in the method based

Fig. 7 Interpretation of adsorption kinetic curves for slab and $\text{Bi} \rightarrow \infty$

on an approximate ordinary differential Eq. 41 one should solve this equation with the condition $\tau = 0$, $\bar{A} = 0$ taking the value of β_1 from Table 1 and values of c_1 , c_2 , c_3 —from Table 3 (for slab). The resulting value of a diffusion coefficient is $D_s = 2.56 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. For this value computational variations of $\bar{A}$ versus τ based on the exact and approximate models were determined. As can be seen from Fig. 7 these two curves are almost indistinguishable. The found value of a diffusion coefficient of cyclohexane in silicalite crystals is consistent with the value designated in [17].

5.2 Adsorption of water on 3A zeolite

In this case, measurements were related to adsorption of water from the vapor mixture of ethanol and water [18]. Spherical zeolite 3A was used as an adsorbent. Measurements were performed at temperature of 105°C under atmospheric pressure. The adsorbent radius was 1.13 mm and the fraction of water in the mixture was 0.257. Zeolite was put on a suspended perforated tray connected to a balance and a stream of the gas phase was flowing around the zeolite with velocity 0.5 ms^{-1} . Adsorption equilibrium was described with the Dubinin-Raduschkevich relation. The dimensionless form of this equation can be expressed as follows:

$$A = B_1 \exp \left[-B_2 \left(\ln \frac{B_3}{Y} \right)^2 \right] \quad (56)$$

where: $B_1 = q_{ms}/q_{mb}$, $B_2 = bT^2$, $B_3 = P_{sat}/(Py_{molb})$, and $Y = y_{mol}/y_{molb} = C/C_b$. Numerical values of individual quantities are as follows: $T = 378 \text{ K}$, $q_{ms} = 0.198 \text{ kg/kg}$, $b = 2.33 \times 10^{-7} \text{ K}^{-2}$. The equilibrium water content in zeolite and a mass transfer coefficient between the gas

Fig. 8 Interpretation of adsorption kinetic curves for slab and $Bi < \infty$

phase and the surface of the pellet were determined by calculations. The following values were obtained: $q_{mb} = 0.183 \text{ kg/kg}$, $k_g = 0.0593 \text{ ms}^{-1}$. The results of measurements are shown in Fig. 8 in the form of symbols. Because of the convective resistance outside the pellet the boundary condition on the surface of the pellet has to be written as

$$\rho_p D_s \left(\frac{\partial q_m}{\partial x} \right)_1 = k_g (C_b - C_1) \quad (57)$$

In dimensionless form:

$$\left(\frac{\partial A}{\partial \eta} \right)_1 = Bi(1 - Y_1) \quad (58)$$

where Bi is a Biot number:

$$Bi = \frac{k_g R_p}{D_s} \cdot \frac{C_b}{q_{mb} \rho_p} \quad (59)$$

where C_b is the concentration of water vapor in the bulk of the gas phase.

The value of Y was determined from the equilibrium Eq. 56. Calculations were conducted using the exact model and the model based on the approximate kinetic equation. In the exact model it was necessary to solve Eq. 13 numerically for $b = 3$ with conditions Eqs. 14, 15 and Eq. 58. A procedure based on the Crank-Nicolson scheme [16] was utilized.

In the approximate model, Eq. 41a was solved with the condition $\tau = 0$, $\bar{A} = 0$, and the dimensionless concentration on the pellet surface A_1 was determined by solving an algebraic equation ($b = 3$):

$$\left[\beta_1^2 + \frac{1}{A_1 \bar{A}} \sum_{j=1}^3 c_j A_1^{2-j} (A_1 - \bar{A})^j \right] \cdot (A_1 - \bar{A}) = 3 Bi (1 - Y_1) \quad (60)$$

resulting from relations Eqs. 41a, 17, 58. Algorithm of calculations was as follows: for a given value of τ the value of $\bar{A}$ was assumed tentatively and A_1 was calculated using formula Eq. 60. Then Eq. 41a was integrated, what led to finding some value of $\tilde{A}$. On the base of values of differences $h = \bar{A} - \tilde{A}$ the value of $\bar{A}$ for which $h = 0$ was found iteratively.

The calculations results are shown in Fig. 8. The resulting diffusion coefficient in micropores is $D_s = 10.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (effective diffusion coefficient referred to an adsorbent pellet of radius $R_p = 1.13 \text{ mm}$). The value of a Biot number corresponding to this value of diffusion coefficient is $Bi = 44$. In Fig. 8 computational courses of kinetic curves corresponding to the exact and approximate models are shown. Both courses are almost identical what confirms the accuracy of the approximate Eq. 41a proposed in this work.

6 Conclusions

1. The approximate kinetic Eq. 41 describes the rate of heat and mass transfer for bodies in the shape of an infinite slab, infinite cylinder and sphere with good accuracy. The relation Eq. 41 is an ordinary differential equation and can be successfully used instead of a partial differential equation which is generally arduous to solve. This is important when a kinetic equation must be solved repeatedly in a complex procedure.
2. The Eq. 41 can be generalized for cases where external transfer resistance occurs in addition to the transfer resistance inside the body. In this case the generalized Eq. 41a should be utilized.
3. Compatibility of the Eq. 41a with the exact solution was tested for a process of radiative cooling of bodies with different shapes. For example, the maximum deviations for the parameter $N_{rc} = 8$ are: 2.2% for a slab, 3.2% for a cylinder, 3.7% for a sphere. The best agreement between the approximate equation and the exact solution occurs for a slab, and the worst—for a sphere.
4. Comparison of the relation Eq. 41a with an LDF equation, which is also a frequently used approximate equation, gives the results favorable for the first one. This is evidenced e.g. in Fig. 6a, b, c and Table 4. Errors that result from applying the approximate equations in relation to exact solutions are presented there.
5. A special feature of the proposed Eqs. 41 and 41a is its high accuracy for short times of the process, what significantly differentiates it from the LDF equation.

6. The proposed kinetic equation was also tested for mass transfer processes. Kinetic curves for typical conditions of adsorption process designated using the exact and approximate models are almost indistinguishable, what indicates that the proposed approximate equation is accurate. This is true for both processes in which the mass transfer resistance in the pellet is predominant and processes in which the resistance is present in both phases of the system.

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Appendix: Model based on approximation of temperature profile with parabolic equation

If the temperature in body center is denoted as T_0 and on body boundary as T_1 one can get:

$$T = T_0 + (T_1 - T_0) \left(\frac{x}{s} \right)^2 \quad (61)$$

When introducing the dimensionless variables A and η one can obtain:

$$A = A_0 + (A_1 - A_0) \eta^2 \quad (62)$$

Equation 10 leads to the result:

$$\bar{A} = b \int_0^1 [A_0 + (A_1 - A_0) \eta^2] \eta^{b-1} d\eta = \frac{2}{b+2} A_0 + \frac{b}{b+2} A_1 \quad (63)$$

Therefore:

$$A_0 = \frac{b+2}{2} \bar{A} - \frac{b}{2} A_1 \quad (64)$$

When differentiating the profile Eq. 62 one can get:

$$\frac{\partial A}{\partial \eta} = 2(A_1 - A_0) \eta \quad (65)$$

The above gradient for body boundary ($\eta = 1$) equals:

$$\left(\frac{\partial A}{\partial \eta} \right)_1 = 2(A_1 - A_0) = (b+2)(A_1 - \bar{A}) \quad (66)$$

where the relation Eq. 64 is included.

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