
THE SHELL PROGRESSIVE MODEL OF ADSORPTION IN A SINGLE PARTICLE

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A model is formulated of nonisothermal adsorption in a single sorbent particle on the assumption that the adsorption takes place in terms of a so-called "shell-progressive" mechanism, external heat transfer only being considered. The model results are compared with experimental ones and with those of diffusion model formulated by us previously.

In our previous works¹⁻⁵ we have presented the model of nonisothermal adsorption in a single sorbent particle. In that model the internal diffusion was described by Fick's law and heat transfer in a particle by Fourier's law. We did not consider the external mass transfer but only the external heat transfer. The model equations thus represent a set of strongly nonlinear parabolic partial differential equations whose solution is much time-consuming. This fact led us to the formulation of a simplified model^{1,5} in which we assumed constant particle temperature (external heat transfer only was considered). A comparison with experiment² showed adequacy of that simplified model. The time of computation was essentially shorter, however, still too high to be able to employ that model of particle for calculating an adsorber on the basis of heterogeneous model. The time of computation can be substantially reduced by using the method of orthogonal collocation⁶.

The effort to obtain a model of adsorption in a single particle as simple as possible led us to a so-called "shell progressive" model which corresponds to the shrinking core model in noncatalytic reactions fluid-solid phase when the rate of process is determined by the diffusion through a shell.

THEORETICAL

When deriving the model, the following simplifying assumptions were introduced: 1) A one-component gas phase is considered, *i.e.* the external mass transfer may be neglected. 2) The spherical sorbent particles which consist of a core without adsorbate enveloped by a shell with an equilibrium concentration of adsorbate. 3) The rectangular adsorption isotherm, linear dependence of equilibrium concentration of ad-

sorbate on temperature. 4) The concentration profile is at each moment the same as in steady-state diffusion between the particle surface and core surface (a so-called quasistationary state). 5) The heat transfer resistance is concentrated only in the external film. 6) The heat of adsorption and specific heat capacity are independent of temperature.

The rate of diffusion of an adsorptive through a spherical surface of radius $r \in \langle r_j, R \rangle$ is

$$\dot{\xi} = 4\pi r^2 D \, dc/dr. \quad (1)$$

By integrating under the boundary condition $r = r_j$, $c = 0$ and $r = R$, $c = c_0$, we get

$$\dot{\xi} = 4\pi D c_0 r_j R / (R - r_j). \quad (2)$$

This rate equals the rate of adsorption. The total amount adsorbed in a particle is

$$A = (4/3) \pi a (R^3 - r_j^3), \quad (3)$$

from which

$$\frac{dA}{dt} = -4\pi r_j^2 a \frac{dr_j}{dt} + \frac{4}{3} \pi (R^3 - r_j^3) \frac{da}{dt} \quad (4)$$

and consequently

$$D c_0 \frac{r_j R}{R - r_j} = -r_j^2 a \frac{dr_j}{dt} + \frac{1}{3} (R^3 - r_j^3) \frac{da}{dt}. \quad (5)$$

On inserting the dimensionless variables

$$\varphi = r/R; \quad \varphi_j = r_j/R; \quad Q = c/c_0; \quad q = a/a_0; \quad \tau = t/t^0, \quad (6)$$

where

$$t^0 = R^2 a_0 / (D c_0) \quad (7)$$

and rearranging, we get

$$\frac{d\varphi_j}{d\tau} = \frac{1}{3q} \frac{1 - \varphi_j^3}{\varphi_j^2} \frac{dq}{d\tau} - \frac{1}{q \varphi_j (1 - \varphi_j)}. \quad (8)$$

On the assumption of a linear dependence of the adsorbate concentration on temperature and linear adsorption isotherm, *i.e.*

$$\begin{aligned} c &= 0, & a &= 0 \\ c &> 0, & a &= b_0 - b_1 T, \end{aligned} \quad (9)$$

or in a dimensionless form

$$\begin{aligned} Q &= 0, \quad q = 0 \\ Q &> 0, \quad q = 1 - \beta\Theta, \end{aligned} \quad (10)$$

where

$$\Theta = \frac{(T - T_0) \rho c_p}{(-\Delta H) a_0}, \quad \beta = \frac{(-\Delta H) b_1}{\rho c_p}, \quad (11)$$

it is possible to arrange Eq. (8) into the form

$$\frac{d\varphi_j}{d\tau} = \frac{1 - \varphi_j^3}{\varphi_j^2} \frac{(-\beta)}{3(1 - \beta\Theta)} \frac{d\Theta}{d\tau} - \frac{1}{1 - \beta\Theta} \frac{1}{\varphi_j(1 - \varphi_j)}. \quad (12)$$

For the mean concentration of adsorbate in a particle it holds

$$\bar{q} = (1 - \varphi_j^3) q. \quad (13)$$

The profile of dimensionless concentration of adsorptive in a particle, Q , is obtained by solving the equation

$$\nabla^2 Q = 0 \quad (14)$$

under the boundary conditions

$$\begin{aligned} \varphi &= \varphi_j, \quad Q = 0 \\ \varphi &= 1, \quad Q = 1. \end{aligned}$$

By solving Eq. (14) we get

$$Q = 1 - \frac{\varphi_j(1 - \varphi)}{\varphi(1 - \varphi_j)}. \quad (15)$$

The equation of enthalpy balance under the given assumptions¹ is

$$\frac{4}{3} \pi R^3 \rho c_p \frac{dT}{dt} = 4\pi R^2 (-\Delta H) D \left(\frac{dc}{dr} \right)_{r=R} - 4\pi R^2 h(T - T_0), \quad (16)$$

or in dimensionless form

$$\frac{d\Theta}{d\tau} = 3 \left(\frac{dQ}{d\varphi} \right)_{\varphi=1} - \omega\Theta, \quad (17)$$

where

$$\omega = \frac{3a_0 R h}{c_0 \rho c_p D}. \quad (18)$$

From Eq. (15) we get

$$\left(\frac{dQ}{d\varphi}\right)_{\varphi=1} = \frac{\varphi_J}{1 - \varphi_J} \quad (19)$$

On inserting into the enthalpy balance (17)

$$\frac{d\Theta}{d\tau} = 3 \frac{\varphi_J}{1 - \varphi_J} - \omega\Theta \quad (20)$$

The model is described by two ordinary differential equations (12) and (20) and the initial condition

$$\tau = 0; \quad \varphi_J = 1; \quad \Theta = 0. \quad (21)$$

The equations were solved numerically by the Runge-Kutta 2nd order method.

As a limiting case it is possible to present the model for $\beta = 0$, *i.e.* when the equilibrium adsorbate concentration does not depend on temperature. Then Eq. (12) simplifies to

$$\frac{d\varphi_J}{d\tau} = - \frac{1}{\varphi_J(1 - \varphi_J)} \quad (22)$$

whose solution is obtained in closed form

$$\tau = \frac{1}{6} - \frac{\varphi_J^2}{2} + \frac{\varphi_J^3}{3} \quad (23)$$

The model is then described by Eqs (20) and (23) and by initial conditions (21).

EXPERIMENTAL

The dependence of temperature and adsorbed amount was measured in a gravimetric sorption apparatus GRAVIMAT which was completed by a device for measuring temperature on the surface and in the middle of particle². The scheme of the equipment is given in Fig. 1. As an adsorbent, the molecular sieve Calsit 5A produced by VÚRUP Bratislava (spherical particles about 1 cm in diameter) was used. n-Heptane, chromatographically pure was chosen as an adsorptive. In each measurement, two sorbent particles were placed in the apparatus, one in order to measure adsorbed amount and the second for measuring temperatures. The temperature inside the particle was measured by two iron-constantan thermocouples of diameter 0.1 mm. One was placed in the middle of the particle and the second fixed on its surface.

The maximum temperature was reached approximately after two minutes and afterwards a slow process of cooling the particle followed.

In this work, the presented measurement was carried out at an initial temperature of 75°C and vapour pressure of n-heptane $2 \cdot 10^3$ Pa. The difference between the temperature of particle

and that of its environment was as much as 25°C, whereas the difference between the surface and centre of particle was not higher than 5°C.

The values of physical parameters are as follows: $\rho = 1\,040\text{ kg m}^{-3}$, $c_p = 963\text{ J kg}^{-1}\text{ K}^{-1}$, $R = 0.526$ and 0.547 cm , $c_0 = 0.6912\text{ mol m}^{-3}$, $a_0 = 1\,314.5\text{ mol m}^{-3}$, $(-\Delta H) = 41\,570\text{ J. mol}^{-1}$ and equilibrium relation (9)

$$a = 2\,327.9 - 3.41T.$$

RESULTS AND DISCUSSION

Model equations (12) and (20) contain two dimensionless parameters β and ω . The value of parameter β can be calculated on the basis of the physical parameters given above. The values of diffusion coefficient and heat transfer coefficient, however, are not known beforehand and therefore the parameter ω was determined on the basis of agreement of the measured and calculated dependences of temperature and adsorbed amount. Analogously for converting the dimensionless time τ to time t it is necessary to know the characteristic time t^0 which is defined by Eq. (7). Since the value of diffusion coefficient occurs in it, it was determined on the basis of agreement of time dependence \bar{q} . For $\omega = 15$ the value of characteristic time $t^0 = 1.343$.

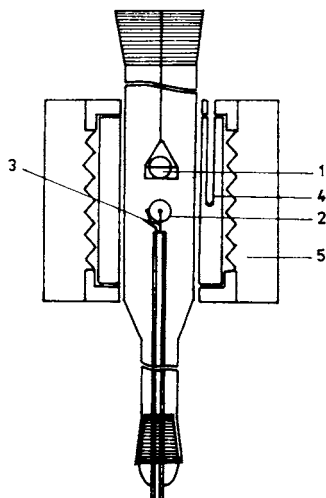


FIG. 1

Scheme of experimental equipment. 1 Suspended particle in which the adsorbed amount was observed, 2 particle in which temperature was measured, 3 thermocouples, 4 temperature control, 5 electric oven

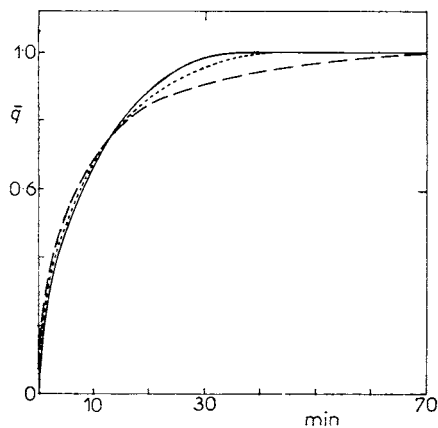


FIG. 2

Dependence of mean dimensionless concentration of adsorbate \bar{q} on time. — Experiment, - - - shell model ($\omega = 15$, $\beta = 0.142$), - · - · shell model ($\omega = 25$, $\beta = 0.142$)

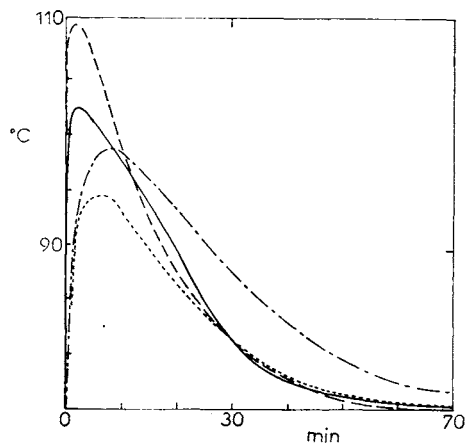


FIG. 3

Dependence of temperature on time. — Experiment, - - - shell model ($\omega = 15$, $\beta = 0.142$), ····· shell model ($\omega = 25$, $\beta = 0.142$), - · - · diffusion model

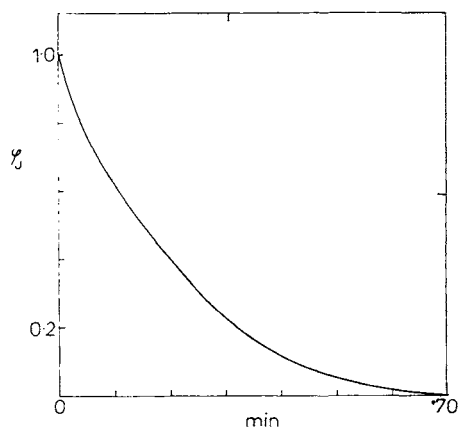


FIG. 4

Dependence of dimensionless radius of core on time ($\omega = 15$, $\beta = 0.142$)

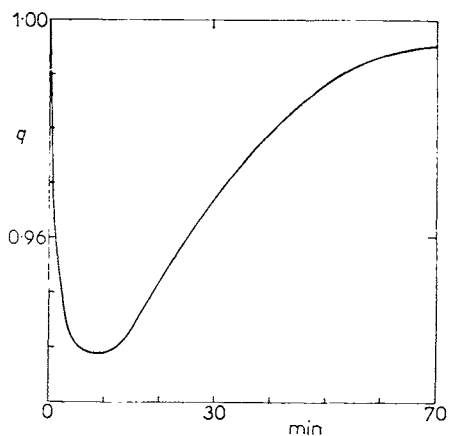


FIG. 5

Dependence of adsorbate concentration in shell on time ($\omega = 15$, $\beta = 0.142$)

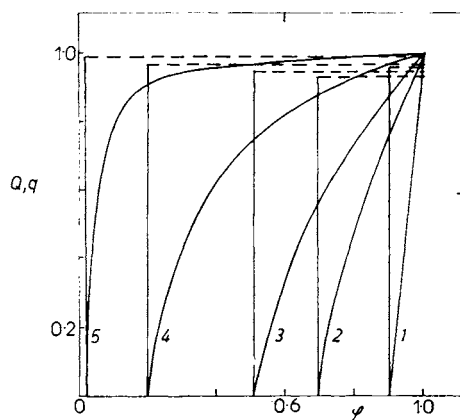


FIG. 6

Profiles of dimensionless concentrations of adsorbate q and adsorptive Q at time intervals 1 1, 2 7.8, 3 18, 4 36, 5 65 min; - - - adsorptive, — adsorbate ($\omega = 15$, $\beta = 0.142$)

. 10^4 s, which corresponds to $D = 3.92 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Then the heat transfer coefficient calculated from Eq. (18) is $1.96 \cdot 10^{-4} \text{ J m}^{-2} \text{ s}^{-1} \text{ K}^{-1}$.

Comparison of the measured adsorbed amount with that calculated in terms of the shell model is depicted in Fig. 2. In Fig. 3 comparison of the course of temperatures, both measured in the centre of particle and calculated according to the shell model (for $\omega = 15$ and $\omega = 25$) and the diffusion model¹, is given. In next figures there are the time dependences of core radius (Fig. 4) and dimensionless concentration of adsorbate in the shell (Fig. 5) and the profiles of dimensionless concentrations of adsorbate and adsorptive in the particle in several time intervals (Fig. 6). The comparison of the temperature course for $\omega = 15$ and $\beta = 0.142$ and $\beta = 0$, i.e. for the case of constant adsorbate concentration, is plotted in Fig. 7.

The shell-progressive model of nonisothermal adsorption in a single sorbent particle as described in this work represents fairly well the given process which is evidenced by comparison with experimental results. The best agreement was attained for the value of parameter $\omega = 15$ and on considering the linear dependence of the adsorbate concentration on temperature. A relatively good agreement is also yielded by the simplified model for $\beta = 0$. We did not reach better agreement than that on using the diffusion model but the model equations are in this case much simpler and therefore the time of computation is essentially shorter. The shell model contains only two parameters, β and ω , whereas the diffusion model contains six parameters. Moreover, for small values of parameter β , the dependence of the adsorbate concentration on temperature may be eliminated, and then we get the solution of mass balance in a closed form.

On the basis of the results presented it is possible to judge that the shell progression model of nonisothermal adsorption in a single sorbent particle can be used for calculating the absorber on the basis of heterogeneous model.

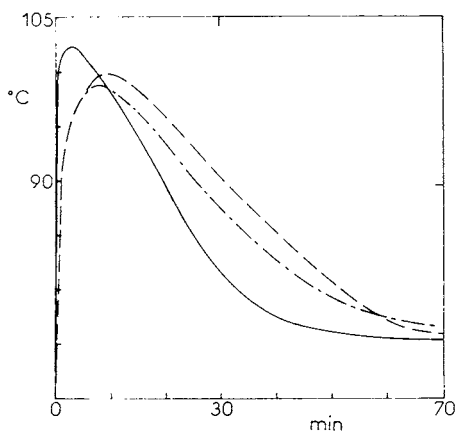


FIG. 7

Dependence of temperature on time. — Experiment, - - - - shell model ($\omega = 15$, $\beta = 0.142$), - · - · shell model ($\omega = 15$, $\beta = 0$)

LIST OF SYMBOLS

a	adsorbate concentration (mol m^{-3})
a_0	equilibrium adsorbate concentration at a temperature T_0 (mol m^{-3})
A	adsorbed amount (mol)
b_0, b_1	coefficients in Eq. (9) (mol m^{-3}), ($\text{mol m}^{-3} \text{K}^{-1}$), resp.
c	adsorptive concentration (mol m^{-3})
c_0	adsorptive concentration in bulk flow (mol m^{-3})
c_p	specific heat capacity of sorbent ($\text{J kg}^{-1} \text{K}^{-1}$)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
h	heat transfer coefficient ($\text{J m}^{-2} \text{s}^{-1} \text{K}^{-1}$)
$(-\Delta H)$	heat of adsorption (J mol^{-1})
q	dimensionless concentration of adsorbate in particle
Q	dimensionless adsorptive concentration in gas phase
r	radial coordinate (m)
r_j	core radius (m)
R	particle radius (m)
t	time (s)
t^0	characteristic time defined by Eq. (7) (s)
T	temperature (K)
T_0	temperature of bulk flow of gas (K)
β	dimensionless parameter of Eq. (10)
φ	dimensionless radial coordinate
φ_j	dimensionless core radius
ξ	diffusion rate (mol s^{-1})
τ	dimensionless time
Θ	dimensionless temperature rise
ρ	density of sorbent particle (kg m^{-3})
ω	dimensionless parameter defined by Eq. (18)

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