

ANALYSIS OF ADSORPTION KINETICS ON ZEOLITES UNDER NONISOTHERMAL CONDITIONS.

I. ANALYTICAL SOLUTION OF THE PROBLEM

Milan KOČIŘÍK, Miloš SMUTEK, Arkadij BEZUS and Arlette ZIKÁNOVÁ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 120 00 Prague 2*

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Mass and heat balance equations for a zeolitic compact in the form of an infinite plate were solved and theoretical equations for the kinetic curves were discussed. Besides the general solution obtained by the residuum method, approximate solutions for limiting cases were derived.

Several studies were carried out recently to elucidate the disagreement between the diffusion coefficients obtained from sorption measurements and those measured by the NMR spin echo method¹⁻⁵. Most of this work was carried out on zeolites and in all cases the adsorption kinetics was relatively rapid. The investigation of these rapid processes is experimentally difficult and the heat effects must be either eliminated or involved in the theory. The problem of a simultaneous heat and mass transfer in relation to the measurement of diffusion coefficients was dealt with from different aspects in several communications²⁻¹¹.

The aim of the present work is to find an optimum method of measurement and analysis of kinetic data obtained under nonisothermal conditions. The conditions during measurement of diffusion coefficients should be such that the system behaves practically as a linear one. For this reason the experiments are carried out in steps, the concentration changes of the adsorbate at the external surface of the adsorbent being small. This enables the use of a linear mathematical model, so that, *e.g.*, it is not necessary to consider the temperature dependence of the effective diffusion coefficient for a given kinetic curve. However, the temperature dependence of the equilibrium concentration of the adsorbate cannot be eliminated in this way. This phenomenon plays an important role since the adsorption heat evolved influences the kinetic measurement. The mathematical model described below is fitted for the measurement on thin plates pressed from crystalline zeolites¹. A similar model for circular-shaped pellets was elaborated by Lee and Ruthven³. We shall now derive the complete analytical solution of the problem formulated in the preceding work², which involved only the calculation of statistical moments of the kinetic curves and their dependence on the plate thickness.

MATHEMATICAL MODEL AND ITS SOLUTION

The model is based on the following assumptions: 1) The compact of zeolitic crystallites can be depicted as a system of spherical porous particles of equal size, whose radius is negligible against the thickness of the plate, $2L$. 2) As the mass transfer mechanism, we consider only the flow of the sorbing substance through the intercrystalline space (macropores). We assume that the mass flow density J is given as

$$J = -D_g \text{grad } c_g, \quad (1)$$

where D_g is the coefficient of intercrystalline diffusion based on the permeability of the porous medium¹² and c_g is the concentration of the sorbing substance in the intercrystalline space (in units of amount of substance per unit volume of this space). Hence, we assume that the transport in the crystallites plays no role. 3) With respect to the structure of the sample (*cf.* point 1), we assume that the heat transfer rates decrease in the order: intracrystalline heat transfer > heat transfer in the zeolitic compact > heat dissipation from the plate surface into the surroundings. 4) The steps in the concentration of the sorbing substance $\Delta c_g = c_g - c_{gi}$ in consecutive experiments and the corresponding temperature steps $\Delta T = T - T_i$ in each experiment are sufficiently small so that the changes of the adsorbate concentration $\Delta c_a = c_a - c_{ai}$ can be expressed with a satisfactory accuracy by the linear relation¹³

$$\Delta c_a \approx \varepsilon \Delta c_g - \omega \Delta T, \quad (2)$$

where c_a is the concentration of the sorbing substance in the crystallites (in units of amount of substance per unit volume of crystalline phase), T is the temperature in a given place of the compact, and

$$\varepsilon = (\partial c_a / \partial c_g)_{T_i, c_g = c_{gi}} > 0, \quad \omega = -(\partial c_a / \partial T)_{c_{gi}, T = T_i} > 0. \quad (3), (4)$$

The subscript i denotes the respective initial values of concentration and temperature.

The mass and heat balance equations for a differential layer of the zeolitic compact can be under these assumptions written as

$$\frac{\partial c_g}{\partial t} = \frac{D_g}{\tau_g} \frac{\partial^2 c_g}{\partial x^2} - \frac{1 - \alpha_g}{\alpha_g} \left(\varepsilon \frac{\partial c_g}{\partial t} - \omega \frac{\partial T}{\partial t} \right) \quad (5)$$

$$\rho_p \lambda_p \frac{\partial T}{\partial t} = \lambda_p \frac{\partial^2 T}{\partial x^2} - \Delta H_{ad} (1 - \alpha_g) \left(\varepsilon \frac{\partial c_g}{\partial t} - \omega \frac{\partial T}{\partial t} \right). \quad (6)$$

Here τ_g is a factor involving the effects of tortuosity and variable cross section of pores on diffusion in the pores, α_g is the intercrystalline porosity,

$$\alpha_g = 1 - \rho_p/\rho_z, \quad (7)$$

ρ_p compact density, ρ_z crystallite density, κ_p heat capacity of the compact, λ_p its thermal conductivity, $-\Delta H_{ad}$ differential molar heat of adsorption, x coordinate measured from the plane of symmetry of the plate toward its surface.

The initial and boundary conditions characterizing the kinetic experiment are

$$c_g = c_{gi} \quad \text{for } t = 0 \quad \text{and} \quad 0 < x \leq L, \quad (8)$$

$$T = T_i \quad \text{for } t = 0 \quad \text{and} \quad 0 < x \leq L, \quad (9)$$

$$c_g = c_{gi} + \Delta c_{g0} \quad \text{for } t > 0 \quad \text{and} \quad x = L, \quad (10)$$

$$-\lambda_p(\partial T/\partial x) = h(T - T_i) \quad \text{for } t > 0 \quad \text{and} \quad x = L, \quad (11)$$

$$\partial c_g/\partial x = \partial T/\partial x = 0 \quad \text{for } x = 0. \quad (12)$$

Here we denote h the coefficient of heat transfer on the compact surface and Δc_{g0} the step change in concentration of the sorbing substance at the compact at the beginning of the experiment. The ratio of the rates of penetration of the temperature and concentration profiles into the interior of the compact depends on the ratio of D_T/D_{eff} , where

$$D_T = \lambda_p/\kappa_p\rho_p \quad (13)$$

is the so-called temperature diffusivity and

$$D_{eff} = \frac{D_g}{\tau_g} \left(\frac{1 - \alpha_g}{\alpha_g} \varepsilon + 1 \right)^{-1} \approx \frac{D_g}{\tau_g \varepsilon} \frac{\alpha_g}{1 - \alpha_g} \quad (14)$$

is the effective diffusion coefficient of the sorbing substance in the compact.

The range of the parameter D_T/D_{eff} for experiments with zeolitic compacts was estimated with the use of the data for D_{eff} obtained by evaluating our experiments with the cyclohexane-zeolite 13X system using the isothermal model. Typical values of D_{eff} were between 10^{-9} and $10^{-8} \text{ m}^2 \text{ s}^{-1}$. Based on the data $\kappa_p = 0.84$ and $0.92 \text{ J g}^{-1} \text{ K}^{-1}$ for zeolites 5A and 13X (ref.^{14,3}), we chose for the estimation of D_T $\kappa_p = 0.9 \text{ J g}^{-1} \text{ K}^{-1}$ and further $\lambda_p = 5.9 \cdot 10^{-4} \text{ kJ s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$ (ref.¹⁵). Finally, we used $\rho_p = 1000 \text{ kg m}^{-3}$, so that according to Eq. (13) the value of D_T is about

$6-7 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $D_T/D_{eff} = 60-700$. Rough calculations showed that under the condition

$$D_T/D_{eff} > 100 \quad (15)$$

the temperature distribution in the plate can be considered approximately independent of x during the whole process. Thus, the model of the simultaneous mass and heat transfer could be simplified for most of our experiments. When the temperature is independent of x , we obtain from the differential balance (6) by integration over the volume of the plate and using the Gauss-Ostrogradskii theorem the integral balance. After introducing dimensionless parameters and the condition (11) we obtain the following mathematical formulation of the problem:

$$(\partial C_g/\partial \tau) = (\partial^2 C_g/\partial X^2) + (\partial \vartheta/\partial \tau), \quad (16)$$

$$(\partial \vartheta/\partial \tau) + \alpha \vartheta - \beta (\partial C_g/\partial X)_{X=1} = 0, \quad (17)$$

$$C_g = \vartheta = 0 \quad \text{for } \tau = 0 \quad \text{and } 0 \leq X \leq 1, \quad (18)$$

$$C_g = 1 \quad \text{for } \tau > 0 \quad \text{and } X = 1, \quad (19)$$

$$\partial C_g/\partial X = \partial \vartheta/\partial X = 0 \quad \text{for } X = 0. \quad (20)$$

The dimensionless parameters are defined as follows:

$$C_g = \Delta c_g/\Delta c_{g0}, \quad \vartheta = -\frac{\Delta T(\partial c'_a/\partial T)_p}{\Delta c_{g0}(\partial c'_a/\partial c_g)_T}, \quad (21), (22)$$

$$X = x/L, \quad \tau = D_{eff}t/L^2, \quad (23), (24)$$

$$\alpha = hL/D_{eff}\rho_p\kappa_p, \quad \beta = \Delta H_{ad}(\partial c'_a/\partial T)_p/\kappa_p, \quad (25), (26)$$

and c'_a is the concentration of the sorbing substance in the crystallites, expressed in units of amount of substance per mass unit of the sorbent (compare the definition of c_a in Eq. (2)).

By application of the Laplace transform on Eqs (16) and (17) with boundary conditions (18)–(20) and solving the resulting ordinary differential equations we obtain the Laplace transform $\tilde{\gamma}(P)$ of the kinetic curve $\gamma(\tau)$ defined by²

$$\tilde{\gamma}(t) = \Delta m(t)/\Delta m(\infty) \quad (27)$$

as the relative saturation of the sorbent, where $\Delta m(t)$ and $\Delta m(\infty)$ are the mass increments of the zeolitic compact from the beginning of the experiment up to a time t and up to the equilibrium, respectively. The solution in the Laplace domain is

$$\tilde{\gamma}(P) = \frac{1}{P} \frac{\operatorname{tgh}(\sqrt{P})/\sqrt{P}}{1 + f(P) \operatorname{tgh}(\sqrt{P})/\sqrt{P}}, \quad (28)$$

where P is a complex variable and

$$f(P) = \beta P / (P + \alpha). \quad (29)$$

The inversion formula for the Laplace transform is¹⁶.

$$\gamma(\tau) = \lim_{b \rightarrow \infty} \frac{1}{2\pi i} \int_{a-ib}^{a+ib} \exp(P\tau) \tilde{\gamma}(P) dP. \quad (30)$$

The function $\tilde{\gamma}(P)$ has exclusively simple poles, and this for $P_0 = 0$ and $P_n = -q_n^2$, where $q_n(\alpha, \beta)$ are the roots of the transcendental equation

$$\beta q_n \operatorname{tg} q_n = \alpha - q_n^2, \quad n = 1, 2, \dots \quad (31)$$

For $\beta = 0$ (isothermal case) we have $q_n(\alpha, 0) = (2n - 1)\pi/2$ and it can be shown that the following inequalities apply:

$$q_n(\alpha, 0) < q_n(0, \beta) < q_{n+1}(\alpha, \beta); \quad (32)$$

$q(\alpha, \beta)$ has, as compared with the other two cases, one more root for $q_1 < \pi/2$. With increasing n , the roots approach the limiting value of $(2n - 1)\pi/2$.

The solution for the integral (30) is

$$\gamma(\tau) = \sum_{k=0}^{\infty} \exp(P_k \tau) \operatorname{Res} \tilde{\gamma}(P_k) \equiv \sum_{k=0}^{\infty} \exp(-q_k^2 \tau) \operatorname{Res} \tilde{\gamma}(q_k), \quad (33)$$

where the residuums for the individual poles are given as

$$\begin{aligned} \operatorname{Res} \tilde{\gamma}(P_n) &= \lim_{P \rightarrow P_n} \frac{(P - P_n) \operatorname{tgh}(\sqrt{P})/\sqrt{P}}{P[1 + f(P) \operatorname{tgh}(\sqrt{P})/\sqrt{P}]} = \\ &= - \lim_{q \rightarrow q_n} \frac{(q_n^2 - q^2) (\operatorname{tg} q)/q}{q^2 [1 + f(q) (\operatorname{tg} q)/q]}. \end{aligned} \quad (34)$$

For $P_0 = 0$ we have immediately

$$\text{Res } \tilde{\gamma}(0) = 1/(1 + f(0)), \quad (35)$$

where $f(0) = \beta$ for $\alpha = 0$ (i.e., for $hL \ll D_{\text{eff}} \rho_p x_p$) and $f(0) = 0$ for $\alpha \neq 0$. For other poles we obtain by using l'Hospital's rule and Eq. (31):

$$\text{Res } \tilde{\gamma}(P_n) \equiv \text{Res } \tilde{\gamma}(q_n) = - \frac{2(1 - \alpha/q_n^2)^2}{q_n^2(1 - \alpha/q_n^2)^2 + \beta(1 + \alpha/q_n^2) + \beta^2}. \quad (36)$$

Thus, Eq. (33) acquires the form

$$\gamma(\tau) = \frac{1}{1 + f(0)} - 2 \sum_{n=1}^{\infty} \frac{(1 - \alpha/q_n^2)^2 \exp(-q_n^2 \tau)}{q_n^2(1 - \alpha/q_n^2)^2 + \beta(1 + \alpha/q_n^2) + \beta^2}. \quad (37)$$

DISCUSSION

The series (37) converges rapidly: even for the dimensionless time $\tau = 0.01$ we obtain the value of $\gamma(\tau)$ from the first ten terms with an accuracy better than $2 \cdot 10^{-7}$. Some special cases can be derived from this general formula:

a) For $\beta = 0$, we obtain the solution for isothermal diffusion into the plate¹⁷. As can be seen from Eq. (37), in this case the value of $\gamma(\tau)$ is independent of α . It is sufficient for a practically isothermal behaviour of the system to fulfil the condition $\beta \ll \pi/2$. An insignificant temperature increase of the pellet can be attained not only by a weak evolution of heat and large heat capacity of the sorbent but also by an efficient exchange of the formed heat with the surroundings, i.e., for a large value of α . This, however, ought to be according to Eq. (37) unrealistically high.

b) For a thermally isolated tablet, we have $h = 0$ and hence $\alpha = 0$. The process is then adiabatic. The series (37) leads to the limiting value for $\tau \rightarrow \infty \lim \gamma(\tau) = 1/(1 + \beta)$ instead of 1 as required by the definition (27). This is due to the fact that the definition (27) requires the same final and initial temperature of the system. The final temperature, however, is under adiabatic conditions higher, which leads to a decrease of the resulting equilibrium concentration. Since we evaluate in practice the relative saturation of the sorbent, it is of advantage to introduce the quantity

$$\gamma(\tau)_{\text{ad}} = \frac{\Delta m(\tau)}{\Delta m(\infty)_{\text{ad}}} = (1 + \beta) \gamma(\tau). \quad (38)$$

Instead of the series (37), we then obtain

$$\gamma(\tau)_{\text{ad}} = 1 - 2 \sum_{n=1}^{\infty} \frac{(1 + \beta) \exp(-q_n^2 \tau)}{q_n^2 + \beta + \beta^2}, \quad (39)$$

which is in formal agreement with the solution of the problem of isothermal diffusion at constant volume and variable pressure^{3,17,18}.

c) In practice, strictly adiabatic regime does not occur. Sufficiently isolated sorption systems, characterized by a small value of α , can however behave quasiadiabatically nearly up to the equilibrium state. This primary process is more or less well separated from the second stage of the quasiequilibrium sorption caused by cooling of the system. An idea about the extent of separation of these two processes can be obtained from Eq. (37). As already mentioned, this series contains for $\alpha \neq 0$ one term more with the parameter $q_1 < \pi/2$. In addition, the difference $q_{n+1}(\alpha, \beta) - q_n(0, \beta)$ decreases with decreasing α and increasing n . Indeed, even for $\alpha = 0.5$ the difference between the third term of the series (37) and the corresponding second term of the kinetic adiabatic curve ($\alpha = 0$) is in the relevant range of τ and β less than 1%. For $\alpha < 0.1$, the nonadiabaticity of the system is influenced practically only by the second term of (37), whose contribution is by up to 5% lower than that of the first term of the adiabatic function. Hence, the cooling stage is described mainly, and for larger time practically exclusively, by the additional first term of the series with the parameter q_1 . It can be shown with the aid of the expansion of $\text{tg } x$ for small values of x that for $\alpha < 0.1$ we have $q_1^2 \approx \alpha/(1 + \beta)$ with an accuracy better than 0.35% and the first term of the series (37) is $[2\beta(1 + \beta)]/[2((1 + \beta)^2 + \alpha\beta)] \exp(-\alpha\tau/(1 + \beta))$. Moreover, if we neglect the contribution of α to this term, we obtain for systems with a slow heat exchange with respect to the adsorption rate the approximate relation

$$\gamma(\tau, \alpha, \beta) \approx \frac{\beta}{1 + \beta} \left[1 - \exp\left(-\frac{\alpha\tau}{1 + \beta}\right) \right] + \gamma(\tau, 0, \beta). \quad (40)$$

For $\tau = 1$, the adiabatic sorption is at least 94% whilst in the range of validity of Eq. (40) (up to $\alpha = 0.1$) the residual sorption proceeds at most to 10%; both stages are hence well separated.

d) Although the series (37) converges rapidly, it does not give illustrative information about the initial course of the function $\gamma(\tau)$. An approximate solution is therefore desirable, which is obtained from the Laplace transform (28) for large P values. Then $\text{tgh } \sqrt{P} \approx 1 - 2[\exp(-2\sqrt{P}) + \exp(-4\sqrt{P}) + \exp(-6\sqrt{P}) + \dots]$ and

$$\tilde{\gamma}(P) \approx \frac{P}{1} \left(\frac{1}{\sqrt{P}} - \frac{\beta}{\alpha + \beta\sqrt{P} + P} \right) \left(1 - \frac{(P + \alpha) \exp(-2\sqrt{P})}{\alpha + \beta\sqrt{P} + P} - \dots \right). \quad (41)$$

Inverse Laplace transforms of the individual terms of this expansion can be obtained with the use of tabulated expressions. It can be shown that for both limiting cases, $\alpha = 0$ (adiabatic) and $\beta = 0$ (isothermal), the first correction term in (41) involving $\exp(-2\sqrt{P})$ gives a contribution to the original smaller than $2\sqrt{(\tau/\pi)}\tau \exp(-1/\tau) : (1 + \beta\tau)^2$ and it can be neglected against the leading term for $\tau < 1/4$. The other correction term, involving $\exp(-4\sqrt{P})$, becomes significant only at about $\tau = 0.5$. Hence, the main term in (41) is sufficient for the discussion of the initial kinetic behaviour of the sorbing system.

We shall introduce the substitutions

$$y = \beta^2\tau, \quad k = \alpha/\beta^2 \quad (42)$$

and the function

$$R(z) = (\sqrt{\pi/2z})(1 - \exp z^2 \operatorname{erfc} z), \quad (43)$$

where z is generally a complex variable. This function can be expanded in series:

$$\begin{aligned} R(z) &= \sum_{j=0}^{\infty} \frac{2^j z^{2j}}{(2j+1)!!} - \frac{\sqrt{\pi}}{2} z \sum_{j=0}^{\infty} \frac{z^{2j}}{(j+1)!} = \\ &= 1 - \frac{\sqrt{\pi}}{2} z + \frac{2z^2}{3} - \frac{\sqrt{\pi}}{4} z^3 + \frac{4z^4}{15} - \dots, \end{aligned} \quad (44)$$

where $(2n+1)!! = 1.3.5 \dots (2n+1)$.

The inverse transformation of the leading term in (41) then gives for the isothermal case:

$$\gamma(\tau) \approx 2\sqrt{(\tau/\pi)}, \quad (45)$$

i.e., the square root dependence on time, valid as a good approximation up to more than a half coverage. For the adiabatic case:

$$\gamma(\tau) \approx 2\sqrt{(\tau/\pi)} R(\beta\sqrt{\tau}), \quad (46)$$

which can be written as $\beta\gamma(y) \approx 2\sqrt{(y/\pi)} R(\sqrt{y})$, we have another type of dependence. It follows from the definition of the arguments y and τ that a plot of $\gamma(t)$ against $\ln t$ gives essentially a single curve with a variable shift along the $\ln t$ axis and a variable scale on the γ axis.

For the general case we obtain

$$\beta\gamma(y) \approx 2\sqrt{(y/\pi)} \left(1 - y \frac{R(A-B) - R(A+B)}{2B} \right), \quad (47)$$

where $A = \sqrt{y}/2$ and $B^2 = y(1 - 4k)/4$. This gives with the use of Eq. (44) the following always real series:

$$\begin{aligned} \beta\gamma(y) \approx & 2 \sqrt{\frac{y}{\pi}} \left[1 - \frac{1}{2} \sqrt{\pi y} + \frac{2}{3} y - \frac{1}{4} \sqrt{\pi(1-k)} y^{3/2} + \frac{4}{15} (1-2k) y^2 - \right. \\ & - \frac{\sqrt{\pi}}{12} (1-3k+k^2) y^{5/2} + \frac{8}{105} (1-4k+3k^2) y^3 - \\ & \left. - \frac{\sqrt{\pi}}{48} (1-5k+6k^2-k^3) y^{7/2} + \dots \right]. \end{aligned} \quad (48)$$

From this expansion we obtain as a special case for $k = 0$ Eq. (46) and for $\beta = 0$ Eq. (45) (hence also $y = 0$). It should be noted that Eq. (48) gives useful results only if $\tau = y/\beta^2 < 1/4$.

e) When the reduced time τ increases, the number of significant terms in (37) decreases; for $\tau > 0.2$, the contribution of the third term is smaller than 0.001; the contribution of the fourth term drops below 0.001 already for $\tau > 0.06$. Hence, it has no sense to use the approximate equations for higher values of τ .

The results of the mathematical solution of the simultaneous heat and mass transfer during adsorption on a plate-shaped adsorbent will be used in our further work for numerical calculation of theoretical characteristics, delimitation of the validity region of the solution, and developing a method of evaluation of the kinetic parameters from experimental curves.

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