

Adsorption kinetics and the Planck—Fokker equation*

M. KOČIŘÍK

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague*

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The mass transport in porous adsorbent is interpreted for linear adsorption isotherm and concentration independent diffusion coefficient on the basis of random motion of a single particle of adsorbate. The wandering of particle is regarded as a Markov process which can be described under some simplifying conditions by the Planck—Fokker equation. A relationship between the macroscopically measured kinetic curve or its statistical moments and the quantities characterizing the motion of micro-particle is presented. The adsorption process is interpreted as a process involving the desorption of vacancies.

Для линейной изотермы адсорбции и для диффузионного коэффициента, который не зависит от концентрации, объясняется перенос вещества в пористом адсорбенте на основе случайного движения одной частицы адсорбированного вещества. Блуждание частицы считается процессом Маркова который при некоторых упрощающих условиях описывается уравнением Планка—Фоккера. Приводится соотношение между макроскопически измеренной кинетической кривой или же ее статистическими моментами и величинами, характеризующими движение микрочастицы. Процесс адсорбции в данном случае рассматривается как процесс десорбции вакансий.

This paper is concerned with some basic problems of the mass transport in porous media. As known, there is a number of theoretical approaches to the description of transport phenomena, ranging from pure macroscopic to pure microscopic treatments. The mass transport in porous adsorbents, however, represents a phenomenon complicated to such an extent that so far only an integral view on a phenomenological level could be achieved. As to a detailed description, there is a tendency to apply the knowledge of individual transport mechanisms obtained for geometrically most simple types of channels to the systems which often have an extremely complicated structure with a pronounced effect of the complicated field of adsorption forces.

In the subsequent approach the mechanistic ideas are replaced by some intuitive assumptions: in spite of some drawbacks this approach was found to be of a good use especially for the systems with essential structural inhomogeneities and corres-

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ponding inhomogeneities in force interaction. This proceeding is based on the ideas of *Pontryagin, Andronov, and Vitt* [1] as well as *Tunickii* [2, 3]. This approach is based on the assumption that the wandering of a particle in porous medium is consistent with a so-called Markov process, *i.e.* such a process for which the following correlation between the two successive states of the system exists: the probability of a certain state in subsequent moment depends only on the state of the system in a given moment and is independent of the previous states of the system. Therefore if we know the state of the system at time t_0 , we may predict the probability of a certain state of the system in an arbitrary subsequent time. In our case, the system is consistent with a wandering particle and the state of the system is, therefore, given by the vector \mathbf{x} determining the position of this particle in space. The solution of the problem of a wandering particle requires to find out the probability density $P[\mathbf{x}(t)|\mathbf{x}(0)]$; hence $P[\mathbf{x}(t)|\mathbf{x}(0)] d\mathbf{x}$ is the probability that at time t the components of a random quantity \mathbf{x} will fall into the intervals $(x_1, x_1 + dx_1)$, $(x_2, x_2 + dx_2)$, and $(x_3, x_3 + dx_3)$ provided the initial position of the particle is $\mathbf{x}(0)$. This Markov probability of the transition of a system from the state $\mathbf{x}(0)$ to $\mathbf{x}(t)$ is described by the following equation [4]

$$P[\mathbf{x}(t)|\mathbf{x}(0)] = \int P[\mathbf{x}(t)|\mathbf{x}'(\tau)] P[\mathbf{x}'(\tau)|\mathbf{x}(0)] d\mathbf{x}', \tag{1}$$

where τ is arbitrary time fulfilling the condition

$$t \geq \tau \geq 0. \tag{2}$$

Smoluchowski [5] was perhaps the first to use eqn (1). This relation represents the equation of continuity for the Markov process and it reflects the fact that the probability of the transition from the state $\mathbf{x}(0)$ to $\mathbf{x}(t)$ may be expressed by means of the probability of the transition from $\mathbf{x}(0)$ to arbitrary $\mathbf{x}'(\tau)$ multiplied by the probability of the transition from $\mathbf{x}'(\tau)$ to $\mathbf{x}(t)$. The application of the above equation is too complicated and, therefore, suitable simplifying assumptions are to be introduced.

One of the possibilities is as follows: Equation (1) is transcribed in such a way that t and τ differ by a very small value, *i.e.* the denotation in the original equation changes in the following way

$$P[\mathbf{x}(t + \Delta t)|\mathbf{x}(0)] = \int P[\mathbf{x}(t + \Delta t)|\mathbf{x}'(t)] P[\mathbf{x}'(t)|\mathbf{x}(0)] d\mathbf{x}'. \tag{3}$$

Then the subsequent assumptions on the moments of the function $P[\mathbf{x}(t + \Delta t)|\mathbf{x}'(t)]$ are adopted

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int (x_i - x'_i) P[\mathbf{x}(t + \Delta t)|\mathbf{x}'(t)] d\mathbf{x}' = A_i(\mathbf{x}), \tag{4}$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int (x_i - x'_i)(x_j - x'_j) P[\mathbf{x}(t + \Delta t)|\mathbf{x}'(t)] d\mathbf{x}' = B_{ij}(\mathbf{x}), \tag{5}$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int (x_i - x'_i)(x_j - x'_j)(x_k - x'_k) P[\mathbf{x}(t + \Delta t)|\mathbf{x}'(t)] d\mathbf{x}' = 0. \tag{6}$$

It is also assumed that all moments of higher orders are equal to zero. Under these conditions the Smoluchowski equation may be transformed into the following partial differential equation [6]

$$\frac{\partial P}{\partial t} = - \sum_{i=1}^3 \frac{\partial(A_i P)}{\partial x_i} + \frac{1}{2} \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial^2(B_{ij} P)}{\partial x_i \partial x_j}. \quad (7)$$

This equation is called the Planck–Fokker equation. In order to make further considerations more conceivable we shall concentrate on a special case when:

a) the wandering particle is not subjected to any forces originating outside a granule of adsorbent, *i.e.*

$$A_i = 0, \quad (8)$$

b) the medium is considered to be isotropic, *i.e.*

$$B_{ij} = 2B \delta_{ij}, \quad (9)$$

where δ_{ij} is the Kronecker delta and B is some function of position. Thus the Planck–Fokker equation assumes the form

$$\frac{\partial P}{\partial t} = \frac{\partial^2(BP)}{\partial x_1^2} + \frac{\partial^2(BP)}{\partial x_2^2} + \frac{\partial^2(BP)}{\partial x_3^2}. \quad (10)$$

In the following eqn (10) is used for the description of the random motion of a particle of adsorbate in a porous adsorbent provided the desorption into vacuum takes place. Since P is the conditioned probability of the existence of a particle in the position \mathbf{x} at time t provided this particle was in the position $\mathbf{x}(0)$ at $t = 0$, the determination of an explicit expression of P is stimulated by the solution of eqn (10) with the following initial condition

$$P(\mathbf{x}, 0) = \delta(\mathbf{x} - \mathbf{x}(0)). \quad (11)$$

The symbol $\delta(\mathbf{x} - \mathbf{x}(0))$ stands for the Dirac function. Furthermore we shall take into consideration that a particle of adsorbate which has reached the point \mathbf{x}_s on the surface S of a granule of adsorbate is immediately removed into vacuum, and thus it is no longer free to move randomly. Therefore the surface S functions as a so-called absorption barrier and obeys the boundary condition

$$P(\mathbf{x}_s, t) = 0. \quad (12)$$

The solution of this problem for the given type of region with respect to the position of the point $\mathbf{x}(0)$ is of particular importance and is, therefore, denoted by the symbol $G(\mathbf{x}, t) = G(\mathbf{x}|\mathbf{x}(0))$. It enables us to extend the solution of the problem to more complicated cases when at the beginning of experiment the particle can be found with non-zero probability in several points of the region. The above-mentioned probabilities cannot be used for a direct confrontation with the current kinetic experiment. For this reason, it is necessary to know the probability that a particle which was in the position $\mathbf{x} = \mathbf{x}(0)$ at $t = 0$ desorbs within the time interval $\langle 0, t \rangle$. We shall denote this probability by the symbol $w(t|\mathbf{x}(0))$. As in the time interval $\langle 0, t \rangle$ the particle must either desorb or remain in the adsorbent, the following equation is valid

$$w(t) + \int_V G[\mathbf{x}(t)|\mathbf{x}(0)] d\mathbf{x} = 1, \tag{13}$$

where V is the volume of the region. For other initial conditions G must be replaced by the corresponding solution. For instance, for the case of desorption from a homogeneously saturated granule the particles occur at the beginning of experiment with equal probability in all points of the granule and the general solution $P(\mathbf{x}, t)$ is given by the integration with respect to $\mathbf{x}(0)$ over the total volume of the granule. Hence, it may be written analogously

$$w(t) + \int_V P(\mathbf{x}, t) d\mathbf{x} = 1. \tag{14}$$

Intuitively it may be expected that the conditions of validity of the Planck–Fokker equation are fulfilled only for systems with a linear adsorption isotherm and a diffusion coefficient independent of concentration and therefore only for these systems the results of the description of the random motion of a particle may be confronted with the resultant effect of the motion of a group of particles in their concentration gradient which is established in the measurement of desorption kinetics. Under these conditions it is possible to identify the integral $\int_V P(\mathbf{x}, t) d\mathbf{x}$ (i.e. the probability that a particle does not desorb in the time interval $\langle 0, t \rangle$) with the experimentally established quantity $\gamma(t)$ which stands for the relative saturation of adsorption grain with adsorbate

$$\int_V P(\mathbf{x}, t) d\mathbf{x} = \gamma(t). \tag{15}$$

Similarly, as it is evident from Fig. 1, the probability $w(t)$ is consistent with the complement of $\gamma(t)$ to the unit value.

On the basis of these ideas it is possible to interpret the kinetic curves (used by the author and his co-workers in a series of kinetic studies [7–10]) by means of the quantities characterizing the motion of microparticles. For desorption, the first statistical moment represents the mean desorption time of particles. Analogously the second statistical moment corresponds to the dispersion of the time necessary for a wandering particle to reach the boundary of the region. The case of adsorption can be formally transformed into the previous case in the following way: In conformity with the ideas of *Bering* and *Serpinskii* [11] it may be postulated that a certain amount of vacancies occurs in a particle of the adsorbent which is free from adsorbate. We shall use the symbol $(a_{\square})_{\infty}$ for the concentration of vacancies corresponding to that amount. Furthermore, we shall assume that the adsorption

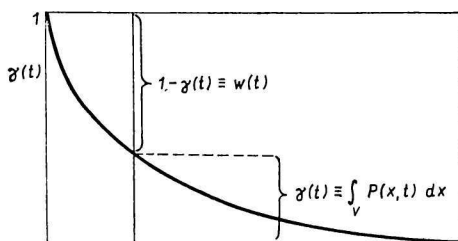


Fig. 1. Kinetic desorption curve in γ vs t coordinates.

The corresponding values $1 - \gamma(t)$ or $\gamma(t)$ characterizes the probabilities that a particle of adsorbate does not desorb in the interval $\langle 0, t \rangle$.

to a certain degree which will be characterized by the concentration of the particles of adsorbate $(a_p)_i$ is accompanied by the desorption of vacancies to the corresponding concentration $(a_\square)_i$. Then it will hold

$$(a_\square)_\infty = (a_\square)_i + (a_p)_i. \quad (16)$$

The adsorption from the level $(i-1)$ to the level i , *i.e.* the conversion of $(a_p)_{i-1}$ into $(a_p)_i$, is accompanied by the desorption of vacancies from the level i to $i-1$, *i.e.* the change from $(a_\square)_i$ to $(a_\square)_{i-1}$. Moreover, it should be realized that the wandering of a given particle is connected with the random motion of the ensemble of vacancies and, *vice versa*, the wandering of a given vacancy is connected with the random motion of the ensemble of particles. Under these assumption we may consider the first moment of the kinetic adsorption curve to be the mean value of the desorption of vacancies or the mean time necessary for a wandering vacancy to reach the boundary of the region. Finally it is worth noticing that in a linear system the corresponding moments for the desorption of particles and vacancies are equal.

References

1. Pontryagin, L., Andronov, A., and Vitt, A., *Zh. Eksp. Teor. Fiz.* **3**, 172 (1933).
2. Tunickii, N. N., private communication.
3. Tunickii, N. N., *Rasshirenyye tezisi dokladov na chetvertoi vsesoyuznoi konferentsii po teoreticheskim voprosam adsorptsii*. (The extended abstracts of papers presented at the 4th USSR conference on the theoretical problems in adsorption.) Ed. 2, p. 99, Moscow, 1973.
4. Weiss, G. H., in *Transport Phenomena in Fluids*. (J. M. H. Howard and M. Dekker, Editors.) New York, 1969.
5. Von Smoluchowski, M., *Ann. Phys.* **21**, 756 (1906).
6. De Groot, S. R. and Mazur, P., *Non-Equilibrium Thermodynamics*. North-Holland Publishing Company, Amsterdam, 1962.
7. Kočířík, M. and Zikánová, A., *Z. Phys. Chem.* (Frankfurt/Main) **71**, 311 (1970).
8. Zikánová, A. and Kočířík, M., *Collect. Czech. Chem. Commun.* **36**, 1225 (1971).
9. Kočířík, M. and Zikánová, A., *Phys. Chem.* (Leipzig) **250**, 250 (1972).
10. Kočířík, M. and Zikánová, A., *Ind. Eng. Chem. Fundam.*, in press.
11. Bering, B. P. and Serpinskiĭ, V. V., private communication.

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