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## DYNAMICS OF SORPTION WITH A RECTANGULAR ISOTHERM AND KINETICS LIMITED BY PARTICLE DIFFUSION\*

R. N. RUBINSTEIN and S. A. SILCHENKO

*V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Vorobjevskoe shosse 47a, Moscow (U.S.S.R.)*

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### SUMMARY

A rigid solution of the problem of sorption dynamics is given for the case of a rectangular isotherm and particle diffusion kinetics. Regions of correctness of the solution are indicated. The initial part of the breakthrough curve has been examined particularly for small sorbent layers, when it was in principle necessary to take into account film diffusion kinetics.

The correctness of the theory and the possible predictions from it are illustrated by the sorption of fulvic acids of natural waters by activated charcoal.

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### INTRODUCTION

The rectangular isotherm reflects the strong interaction between the sorbent and sorbate<sup>1</sup>. This type of isotherm represents the equilibrium in the processes of chemisorption, demineralization of water in mixed layers of ion exchangers<sup>2</sup>, ion exchange with the generalized constant of the exchange

$$\bar{K} = K_{1,2} \left( \frac{a_0}{c_0} \right)^{1/Z_2 - 1/Z_1} \gg 1$$

where  $K_{1,2}$  is the ion-exchange constant for (1) the ion that is absorbed and (2) that is liberated,  $Z_1$  and  $Z_2$  are the charges of the ions,  $a_0$  is the total capacity of the sorbent and  $c_0$  is the concentration of the absorbed ion in the incoming flow<sup>3</sup>, and ion exchange with complexing in the solution<sup>4</sup>. Freundlich's isotherms also could be considered as isotherms of this type. The solutions of the dynamics concerning this isotherm have been considered for kinetics limited by external diffusion<sup>1</sup> and for equilibrium dynamics complicated by longitudinal diffusion<sup>5</sup>. In this paper, this problem is solved for particle diffusion, not previously described in the literature\*\*.

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\*\* After the preparation of this paper for publication, a paper was published<sup>6</sup> in which some special solutions of this problem were discussed (eqn. 12a).

## THEORETICAL

The solution is based on the possibility of using Fick's law for a solid phase. The region in which the solution is acceptable is limited by two conditions:

$$H_1 = \frac{\beta R^2 c_0}{D a_0} \gg 1 \quad \text{and} \quad H_2 = \frac{\beta R^2 v^2 c_0}{D^* D a_0} \gg 1$$

$H_1$  is the criterion, characterizing the relationship between the rates of diffusion in the liquid phase and the solid phase and  $H_2$  is the criterion characterizing the relationship between the rate of diffusion along the flow and the rate of diffusion in the solid phase. In these equations,  $v$  is the linear flow-rate,  $\beta$  is the mass transfer coefficient of the absorbed matter in the mobile phase relative to unit volume,  $R$  is the particle size of the sorbent\*,  $D$  is the diffusion coefficient in the sorbent and  $D^*$  is the longitudinal diffusion coefficient. Estimations and experiments have shown that for many systems these conditions are fulfilled. In particular, these inequalities are found for sorption when the flow-rate is moderate ( $v > 0.1$  cm/sec) from dilute solutions ( $a_0/c_0 > 10^3$ ) with a granular sorbent ( $R > 0.01$  cm) for substances with  $D < 10^{-8}$  cm<sup>2</sup>/sec.

For estimation, it is possible to consider

$$\beta = 3 \cdot 10^{-3} \alpha_1 \cdot \frac{v^{1/2}}{R^{3/2}} \quad (1)$$

where  $\alpha_1$  is the coefficient nearest to unity for aqueous solutions and diffusing particles with low molecular weight, and

$$D^* = 2 \alpha_2 v R$$

where

$$\alpha_2 \approx 1.$$

Apart from the above constraints for small layer thicknesses on the initial part of the breakthrough curve, it is necessary to take into account an instantaneous breakthrough, which is equal to

$$U_m = \frac{c_m}{c_0} = e^{-\frac{\beta l}{v}} \quad (2)$$

where  $l$  is the layer thickness and  $c_m$  and  $U_m$  are dimensional and non-dimensional concentrations, respectively, in the mobile phase at the start of the experiments.

The rectangular isotherm equation in non-dimensional variables is given by<sup>1</sup>

$$\begin{aligned} V < 1; U &= 0 \\ V = 1; U &> 0 \end{aligned} \quad (3)$$

\* For spherical and cylindrical particles  $R$  is the radius, and for flat particles  $R$  is the half-width.

where  $V = a/a_0$  is the non-dimensional mean concentration in the solid phase,  $U = c/c_0$  is the non-dimensional concentration in the liquid (gaseous) phase,  $a$  is the dimensional concentration in the sorbent particles and  $c$  is the dimensional concentration in the mobile phase.

It is clear from eqn. 3 that on the surface of a particle  $V$  can have only two values,  $V = 0$  when  $U = 0$  and  $V = 1$  when  $U > 0$ ; hence, in the region  $U > 0$ , the absorption rate does not depend on  $U$  and therefore there is a limiting length of the layer,  $l$ , which is sufficient to reduce  $U$  from 1 to 0.

Denoting by  $\theta = (D/R^2) [t - (l/\nu)]$  (where  $\nu$  = specific pore volume of the column) the non-dimensional time necessary for the point of the concentration front  $U = 0$  to pass the non-dimensional distance  $X = D l a_0/\nu R^2 c_0$  from the beginning of the layer\*,  $\theta = \theta(X)$ , then for  $T < \theta$ , we have  $V = 0$ , for  $T \geq \theta$  (ref. 7) for spherical particles\*\* we have

$$V = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\pi^2 n^2 (T-\theta)}}{n^2} \quad (4a)$$

for cylindrical particles we have

$$V = 1 - 4 \sum_{n=1}^{\infty} \frac{e^{-\mu_n^2 (T-\theta)}}{\mu_n^2} \quad (4b)$$

and for flat particles we have

$$V = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-\pi^2 (2n+1)^2 (T-\theta)}}{(2n+1)^2} \quad (4c)$$

where the  $\mu$  values are the roots of a Bessel function of the first type, zero order. During the first few moments, only the surface layers of the particles are involved in interactions. This stage is defined by  $\theta \rightarrow 0$  and  $T - \theta \rightarrow 0$  and eqn. 4 is transformed into

$$V = \frac{6}{\sqrt{\pi}} \sqrt{T - \theta} \quad (5)$$

Eqn. 5, contrary to eqn. 4, is true for particles of any form with an arbitrary distribution on  $R$ ; in this case eqn. 5 is defined by the specific surface area of the sorbent,  $R = 3/\omega$ , where  $\omega$  is the surface area of the particles of the sorbent per unit volume.

\* The connection between the dimensional values  $t$  and  $l$  and the non-dimensional values  $\theta$  and  $X$  is easily determined with the aid of an analytical method\* or the transformation of the initial differential equations of the material balance and kinetics<sup>3</sup>.

\*\* For non-equilibrium processes,  $V$  is the mean concentration.

Calculations of  $V(X, T)$  on the basis of eqns. 4 and 5 suggest that the dependence  $\theta(X)$  is known. To define the latter, let us integrate the material balance equation

$$-\frac{\partial U}{\partial X} = \frac{\partial V}{\partial T}$$

from 0 to  $X^*$ :

$$1 = \int_0^{X^*} \frac{\partial V}{\partial T} d\lambda = 6 \sum_{n=1}^{\infty} e^{-\pi^2 n^2 T} \int_0^{X^*} e^{\pi^2 n^2 \theta(\lambda)} d\lambda$$

Introducing a new variable  $\varphi(\theta)$ , which defines the rate of movement of the front with concentration  $U = 0$ :

$$\varphi(\theta) = \frac{dX}{d\theta} \quad (6)$$

we obtain the integral equation with respect to  $\varphi(\theta)$ :

$$\sum_{n=1}^{\infty} \int_0^T e^{-\pi^2 n^2 (T-\theta)} \cdot \varphi(\theta) \cdot d\theta = \frac{1}{6} \quad (7)$$

The solution of this equation gives the required dependence. By applying a Laplace transformation to eqn. 7, we obtain the image  $\varphi(p)$  (refs. 7 and 9):

$$\varphi(p) = \frac{1}{6p} \cdot \frac{1}{\sum_{n=1}^{\infty} \frac{1}{\pi^2 n^2 + p}} = \frac{1}{3(\sqrt{p} \cdot \text{Ctnh} \sqrt{p} - 1)}$$

when  $p \rightarrow 0$ , it corresponds to  $\theta \rightarrow \infty$ ,  $\varphi(p) \rightarrow 1/p$  then  $\varphi(\theta) \rightarrow 1$  or

$$X = \theta + X_0 \quad (8)$$

where  $X_0$  is the constant of integration. This equation follows, in more general form, from the condition of the existence of the asymptotic solution (parallel transfer) when the concentration depends only on one variable,  $\eta = X - T$  (ref. 10).

Then, in accordance with eqn. 4a, we have

$$U = V = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{\frac{\pi^2}{2}(\eta - X_0)}}{n^2}$$

for

$$\eta \leq X_0 \text{ and } U = V = 0$$

for

$$\eta \geq X_0$$

\* The value of the definite integral does not depend on the variable of integration and  $X$  under the integral is replaced with  $\lambda$ .

We can determine  $X_0$  from the material balance equation:

$$\theta = \int_0^X V d\lambda = X - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} + \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\pi^2 n^2 (\theta + X_0)}}{n^2}, \quad \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{90} \text{ (ref. 9)}$$

moreover, for  $\theta > 0.5$ , the last term is less than 1% of the last but one sum, and therefore under parallel transfer conditions  $\theta = X - 1/15^*$ , or, in final form:

$$U = V = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\pi^2 n^2 (X - T - \frac{1}{15})}}{n^2} \quad (9)$$

It should be noted that values of the function

$$F(\tau) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\pi^2 n^2 \tau}}{n^2}$$

have been tabulated<sup>12</sup>.

The solution for small values of  $\theta$  is found by expanding  $\phi(p)$  in a series in  $1/\sqrt{p}$  and  $e^{-\sqrt{p}}$ :

$$\begin{aligned} \phi(p) = \frac{1}{3\sqrt{p}} (1 - 2e^{-2\sqrt{p}} + 2e^{-4\sqrt{p}} - \dots) + \frac{1}{3p} (1 - 4e^{-2\sqrt{p}} + 8e^{-4\sqrt{p}} - \dots) + \\ + \frac{1}{3p^{3/2}} + \frac{1}{3p^{5/2}} + \dots \end{aligned}$$

The original image corresponds to this image

$$\begin{aligned} \varphi(\theta) = \frac{1}{3\sqrt{\pi\theta}} - \frac{2(e^{-1/\theta} - e^{-4/\theta})}{3\sqrt{\pi\theta}} + \frac{1}{3} - \frac{4}{3}\Phi^*\left(\frac{1}{\sqrt{\theta}}\right) + \frac{8}{3}\Phi^*\left(\frac{2}{\sqrt{\theta}}\right) + \\ + \frac{2\sqrt{\theta}}{3\sqrt{\pi}} + \frac{\theta}{3} + \frac{4\theta^{3/2}}{9\sqrt{\pi}} + \frac{\theta^2}{6} + \dots \end{aligned}$$

From this expression, in accordance with eqn. 6 and neglecting in integration the terms less than  $\theta^3$  and  $e^{-1/\theta} \cdot \theta^{3/2+**}$ , we obtain

$$X = \frac{2}{3\sqrt{\pi}} \sqrt{\theta} \left(1 + \frac{2}{3}\theta + \frac{4}{15}\theta^2 - \theta e^{-1/\theta} + \dots\right) + \frac{\theta}{3} \left(1 + \frac{\theta}{2} + \frac{\theta^2}{6} + \dots\right) \quad (10)$$

\* This dependence, written in the form  $t = \frac{a_0 l}{vc_0} - \frac{R^2}{15D}$  is the Shilov equation exactly<sup>11</sup> for  $C = 0$ .

\*\* When  $\theta > 0.5$ , it is not possible to neglect the terms that are more than  $\theta^3$  and  $e^{-1/\theta} \cdot \theta^{3/2}$ ;

$$\Phi^*(\tau) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\tau} e^{-z^2} dz$$

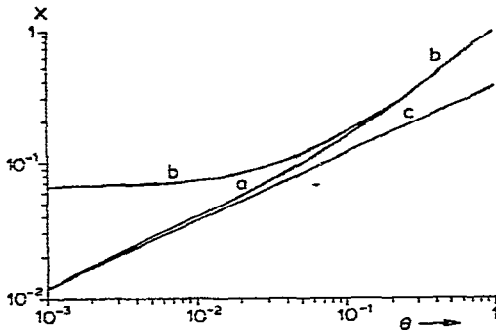


Fig. 1. Dependence of the coordinates of the front point on time for a rectangular isotherm and particle kinetics. (a) The exact solution; (b) the asymptotic solution when  $\theta \rightarrow \infty$ ; (c) the asymptotic solution when  $\theta \rightarrow 0$ .

Comparison of the exact solution (eqn. 10) (Fig. 1, curve *a*) with the asymptotic solution (eqn. 9) (curve *b*) shows that for  $\theta = 0.1$  the difference is approximately 2%; for  $\theta = 0.4$  the asymptotic solution provides an accuracy of better than 0.1%; for  $\theta < 0.01$  the accuracy is better than 1% (curve *c*):

$$X = \frac{2}{3} \sqrt{\frac{\theta}{\pi}} + \frac{\theta}{3} \quad (11)$$

Hence, knowing the dependence  $\theta(X)$ , we obtain

$$U(X, T) = 1 - 6 \sum_{n=1}^{\infty} e^{-\pi^2 n^2 T} \int_0^X e^{\pi^2 n^2 \theta(\lambda)} d\lambda \quad (12)$$

For  $\theta < 0.005$ , remembering that for  $A \rightarrow 0$  the sum  $\sum_{n=1}^{\infty} e^{-n^2 A} \rightarrow \frac{1}{2} \sqrt{\frac{\pi}{A}}$  from eqns. 10 and 11, it is not difficult to deduce for  $T/X^2 \geq 9\pi/4$  that

$$U = 1 - \frac{2}{\pi} \arcsin \frac{3}{2} \sqrt{\frac{\pi}{T}} \cdot X \quad (12a)$$

or

$$U = \frac{2}{\pi} \arctan \frac{2}{3\sqrt{\pi}} \cdot \frac{\sqrt{T - \theta}}{X} \quad (12b)$$

Solving eqn. 12a in respect of  $T/X^2$ , we obtain

$$\frac{T}{X^2} = \left( \frac{\nu R c_0}{T a_0} \right)^2 \cdot \frac{t}{D} = \frac{9\pi}{2} \cdot \frac{1}{1 + \cos \pi U} \quad (12c)$$

In Fig. 2, curve *a* shows the dependence  $V(T)$  for any  $T \geq \theta(X)$ . This curve also gives the approximate dependence  $U(T)$  for  $\theta > 0.2$  ( $X > 0.27$ ). Curve *b* corresponds

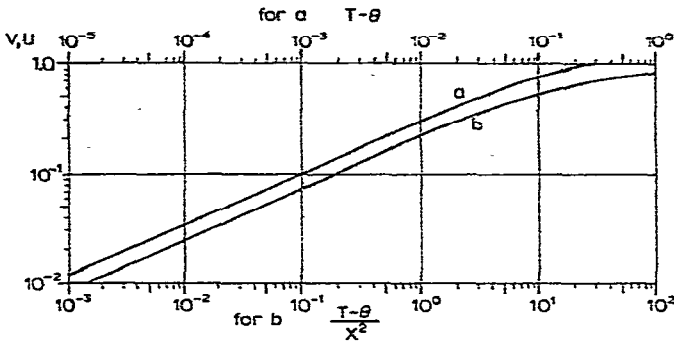


Fig. 2. The breakthrough curves. (a) Concentration in the solid phase for any  $\theta$  and concentration in the liquid phase for  $\theta > 0.2$ ; (b) concentration in the liquid phase for  $\theta < 0.005$ .

to the dependence  $U(T)$  for  $\theta < T < 0.005$  ( $X < 0.028$ ). Here, the start of reading  $T$  begins with the point of breakthrough. The logarithmic scale permits a translation from non-dimensional values  $U$  (or  $V$ ) and  $T - \theta$  to the dimensional values  $c$  (or  $a$ ) and  $(t - t_\theta)^*$ . In order to achieve such a translation, it is necessary to move to the left the point of origin of the coordinates by the value  $\log D/R^2$  for curve  $a$  [or by the value  $\log \left( \frac{v c_0}{l a_0} \right)^2 \cdot \frac{1}{D}$  for curve  $b$ ] and to move it down by the value  $\log c_0$  (or  $\log a_0$ ). Then, superimposing the experimental curves  $\log c$ ,  $\log (t - t_\theta)$  on curve  $a$ , we can determine  $D$  in terms of the difference  $\log (t - t_\theta) - \log (T - \theta)$ . The condition  $\theta > 0.2$  also enables one to find  $a_0$  from eqn. 8 without carrying out a separate experiment. When  $\theta < 0.005$ , the form of the curve is defined by the product  $a_0^2 D$ , and therefore the simultaneous determination of  $a_0$  and  $D$  is impossible.

RESULTS AND DISCUSSION

We shall now illustrate the application of some of the results to the problem of the sorption of "fulvic acids" (FA) by active charcoal (AC).

Some FA were extracted from natural waters by the method described by Forsyth<sup>13</sup> as modified by Sirotkina *et al.*<sup>14</sup> and their concentrations were determined by spectrophotometry<sup>15</sup> and polarography<sup>16</sup>. The active charcoal (type BAU) was subjected to a pre-treatment according to Berezina and Nikolaeva-Fedorovich<sup>17</sup>. Demineralization was effected on type KY-2 cation exchanger. The sorption isotherm obtained in the static experiment is shown in Fig. 3 and it is clear that it is very similar to Freundlich's isotherm, which may be approximated by a rectangular isotherm with  $a_0 = 27$  mg/ml at the concentration level  $c_0 \approx 3 \cdot 10^{-2}$  mg/ml.

As a result of the preliminary estimation of  $D$ , based on the rate of the achievement of the equilibrium in the study of sorption, we obtained a value of  $D \approx 10^{-10}$  cm<sup>2</sup>/sec.

A typical breakthrough curve in the dynamic experiment is shown in Fig. 4 (curve  $a$ ). For these experiments with  $t < 10^4$  sec,  $T < 10^{-2}$  and the curve is therefore described by eqn. 12a.

\*  $t = R^2 T / D$ ;  $t_\theta = R^2 \theta / D$ .

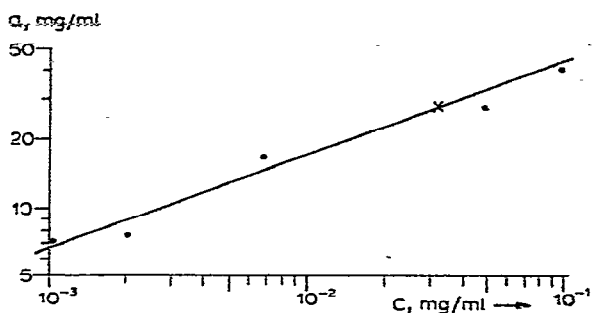


Fig. 3. Sorption isotherm for FA on BAU. Weighed amount, 0.05–2.0 g/ml; bulk weight, 0.15 g/ml; particle diameter, 0.1–0.2 mm; volume of solution of FA, 25 ml; initial concentration of FA, 0.1 mg/ml; active time (time of contact), 25–30 h. Equation of curve:  $a = 107c^{0.4}$ .

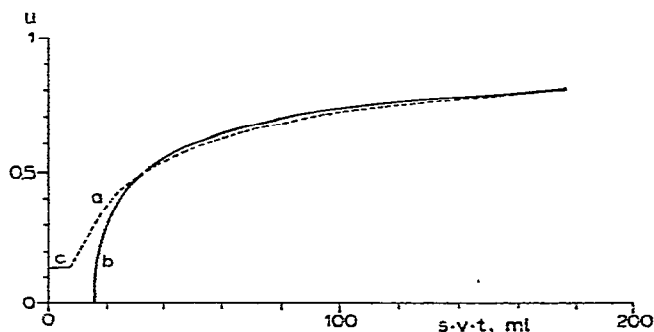


Fig. 4. Comparison of experimental and theoretical breakthrough curves.  $c_0 = 0.031$  mg/ml;  $a_0 = 27$  mg/ml; thickness of layer = 2.3 cm;  $v = 0.22$  cm/sec; particle diameter = 0.2 mm; cross-sectional area of the column ( $s$ ) = 0.09 cm<sup>2</sup>. (a) Experimental points; (b) theoretical breakthrough curve, calculated without taking account of the particle diffusion kinetics; (c) initial part of the breakthrough curve, calculated with taking account of the particle diffusion kinetics.

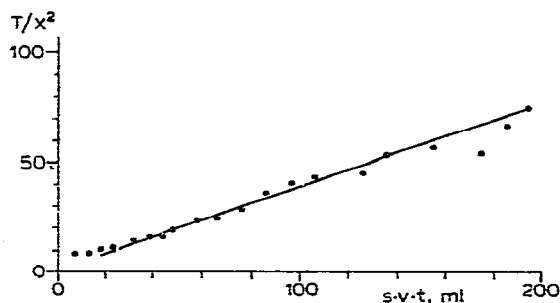


Fig. 5. Dependence of  $T/X^2$  on  $s \cdot v \cdot t$ , constructed on the basis of the experimental curve in Fig. 4.

The term  $a_0 \sqrt{D}$  was determined for each experimental point as follows. For a given value of  $U$  in accordance with eqn. 12c, the value  $T/X^2$  which is proportional to  $s \cdot v \cdot t^*$  was calculated. From Fig. 5, where the dependence  $T/X^2$  on  $s \cdot v \cdot t$  is presented

\*  $s$  = Cross-sectional area of column.



in Cartesian coordinates, it can be seen that the points lie satisfactorily on a straight line that passes through the origin, in accordance with theory.

The value of  $D$ , which was determined from the slope of the line in Fig. 5, was  $1.43 \cdot 10^{-10}$  cm<sup>2</sup>/sec. In Fig. 4 (curve  $b$ ) the theoretical breakthrough curve is shown; it was calculated by means of eqn. 12a for the same system. Initially ( $U < 0.5$ ), the theoretical (calculated) curve (curve  $b$ ) is located to the right of the experimental curve (curve  $a$ ); this difference is easily explained by the occurrence of the instantaneous breakthrough and some deviations of the isotherm from a rectangular form, which are not taken into account in the theory.

We can therefore estimate the effect of the limiting rate of mass transfer from the mobile phase to the surface of the particles, as the solution of the previous problem is strictly valid only for  $H_1 \rightarrow \infty$ . When  $H_1 \neq \infty$  in the initial stages, the concentration on the surface of the sorbent does not have sufficient time to reach equilibrium with  $U$ , and therefore the concentration above it is zero. Hence, the distribution of the layer is accurately described by eqn. 2.

It is known that the concentration distribution  $a_r = a(r/R, T)$  on the cross-section of a spherical particle of radius  $R$ , when the flow  $q_0$  is given to its surface is described by the equation<sup>7</sup>

$$\frac{a_r D}{q_0 R} = 3T + \frac{5r^2/R^2 - 3}{10} - 2 \frac{R}{r} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 T} \cdot \sin \alpha_n r/R}{\alpha_n^2 \cdot \sin \alpha_n}$$

where  $r$  is the distance from the centre of the particle and  $\alpha_n$  is the  $n$ th root of the equation  $\tan \alpha = \alpha$ .

In the front layer  $q_0 = \beta c_0/\omega$  ( $\omega$  is the surface area of the sorbent particles per unit volume), so that for the surface concentration,  $a_r$ , we obtain

$$\frac{a_r}{a_0} = H_1 \left( T + \frac{1}{15} - \frac{2}{3} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 T}}{\alpha_n^2} \right)$$

It follows that the time  $T_0$  that is required in order to reach the value  $a_0$  from the value  $a_r$  in the front layer is determined by the equation

$$\frac{1}{H_1} = T_0 + \frac{1}{15} - \frac{2}{3} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 T_0}}{\alpha_n^2}$$

and the equation for  $T_0 \rightarrow 0$  is

$$T_0 = \frac{9\pi}{4H_1^2}^*$$

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$$\sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} = \frac{1}{10}; \text{ therefore } \frac{1}{15} - \frac{2}{3} \sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 T_0}}{\alpha_n^2} = \frac{2}{3} \sum_{n=1}^{\infty} \frac{1 - e^{-\alpha_n^2 T_0}}{\alpha_n^2} \rightarrow \frac{2}{3} \sqrt{\frac{T_0}{\pi}} \text{ when } T_0 \rightarrow 0.$$

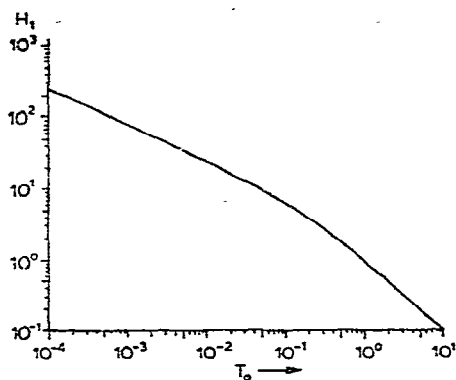


Fig. 6. Dependence of  $T_0$  on  $H_1$ .

(see Fig. 6). For  $T < T_0$ , the concentration beyond the layer on the surface is constant and is determined by eqn. 2.

This provides the possibility of solving the reserve problem of finding  $\beta$  in terms of  $U_m$ .

In particular, if in our example we take for  $U_m$  the first experimental point on curve *a* in Fig. 4, the value  $\beta = 0.16 \text{ sec}^{-1}$  is obtained. A value of  $\beta$  close to this value could be obtained from eqn. 1 when  $\alpha_1 = 1$  ( $\beta = 0.14 \text{ sec}^{-1}$ ). Hence,  $H_1 = 1.2 \cdot 10^2$  and  $T_0 = 5 \cdot 10^{-4}$ , so  $t_0 = T_0 R^2 / D = 350 \text{ sec}$  (or 7 ml). Curve *c* shows the initial part in Fig. 4.

Taking into account the approximate estimation of  $\beta$  (unreliability of the values  $\alpha_1$  (from eqn. 1),  $R$  and  $U_m$ ) the coincidence of the experimental results with the calculated values is reasonably accurate.

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