

## A STUDY OF INTERNAL DIFFUSION DURING THE PHYSICAL ADSORPTION OF BENZENE ON ACTIVE CHARCOAL

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*Dedicated to the 65th anniversary of the late Academician R. Brdička.*

Received June 1st, 1970

Kinetic curves of benzene vapours were measured on active charcoal in the absence of inert gas at a constant pressure of the sorbate around the sorbent granule. A new method was used to evaluate coefficients of internal diffusion from the kinetic curves — a calculation from statistical characteristics of the kinetic curve<sup>1</sup>.

Method of obtaining information on the rate of transfer of adsorbate molecules in a porous adsorbent system from adsorption kinetic measurements have been given considerable attention<sup>2,3</sup>. Our measurements belong to the class of kinetic experiments in which the measured quantity is the total amount of sorbate  $m$  that passes through the outer surface of the adsorbent particle between the beginning of the experiment and a time  $t$  (the  $m-t$  dependence). We chose a method that allows for a direct  $m-t$  determination from the increase of the granule weight with time. The granule is suspended by a quartz spiral. A constant pressure is kept in the environment of the particle during the experiment. Measurements were carried out in the absence of an inert gas. The conditions of the experiments exclude the possibility that the rate of mass transport into the particle could be controlled by the external mass transfer.

The aim of this work was to find an adequate phenomenological description of the kinetics of adsorption of benzene vapour on active charcoal of a known porous structure, over the investigated pressure and temperature range.

The first step necessary in finding the phenomenological description is determining the time dependence on the characteristic dimensions of the sorbent particle of that point on the kinetic curve which corresponds to a certain saturation. For that purpose one chooses a simple, highly symmetric shape of the sorbent particle (a sphere, a cylinder of a finite or infinite length, a plane sheet of infinite dimensions *etc.*). The shape of the particle does not change when the dependence on the characteristic size is determined; *e.g.*, in the case of a cylinder of a finite length, the ratio

radius-length remains constant. One assumes that the sorption material is homogeneous and isotropic. If the dependence holds that the time of a given saturation  $t_\gamma$  is — for a given shape of the particle  $v$  — proportional to the square of the characteristic size  $\lambda_v$ ,

$$t_\gamma = k \cdot \lambda_v^2, \quad (1)$$

then the transport of the sorbate into the sorbent can be described phenomenologically by the formal relation

$$\frac{\partial c}{\partial t} + \frac{\partial n}{\partial t} = \frac{\partial c}{\partial t} (1 + f'(c)) = D \operatorname{div} \operatorname{grad} c \quad (2)$$

whatever the actual transport mechanism might in fact be. The dependence

$$n = f(c) \quad (3)$$

expresses an adsorption isotherm. Here,  $c$  is the sorbate concentration in the volume of adsorbent pores, expressed in grams per a unit of pores volume;  $n$  is the concentration of the adsorbate bound to the solid skeleton of the particle, expressed in grams per a unit of pores volume;  $D$  is a constant characterizing the internal diffusion within the adsorbent particle (it is assumed that  $D$  is independent of the adsorbate concentration).

In order to obtain  $D$  from the kinetic curves, other authors developed methods based on accurate or approximative solutions of the set of equations (2) and (3) with time independent boundary conditions and position independent initial conditions. At the same time, regions over which the concentration  $c$  within the particle varies during the experiment are usually chosen to be small enough to allow for a linearization of equations (2) and (3).

To evaluate the constant  $D$ , the value of the slope of the dependence  $\gamma = (m_t - m_0)/(m_\infty - m_0)$  upon  $t^{1/2}$  in the initial phase of the kinetic curves is often used. Here,  $\gamma$  denotes the relative saturation of the particle and the quantity  $m_t - m_0$  is given by

$$m_t - m_0 = \int_V [n(t) - n(0) + c(t) - c(0)] dV. \quad (3a)$$

Integration goes over the entire volume  $V$  of the adsorbent particle. Using of this method is limited, as it may be used only for small values of time  $t$  (ref.<sup>5</sup>), where the measurements are subjected to fairly large experimental errors.

The second method consists in fitting the experimental curves to exact solutions of the set of equations (2) and (3) with the boundary conditions that correspond to a given shape of the particle<sup>2,3,6</sup>. A coefficient  $f$  is searched which transforms the time coordinate  $t$  of a point of the experimental kinetic curve to a dimensionless time coordinate  $\tau$  of a point of the theoretical curve, both at a given saturation  $\gamma$ . The coefficient  $f$  is thus given by

$$f = \tau/t. \quad (4)$$

In the ideal case the value of  $f$  is independent of saturation regardless of the value  $\gamma$  it was determined for. In practise, however, deviations from the ideal situation occur, and it is difficult to decide which saturation gives the most reliable value of  $f$ . This is important to know, as the value of  $f$  hangs together with the value of the effective coefficient of internal diffusion  $D_e$ . The value of the transformation factor  $f$  at saturation  $\gamma = 0.5$ , used by Timofeev<sup>2</sup>, cannot be regarded as

reliable for fast kinetic processes, where the time coordinate of the point  $\gamma = 0.5$  of the kinetic curve is very small and subjected to a large experimental error.

In this study we attempted to use in evaluation of kinetic experiments the statistical characteristics of the kinetic curves taking into consideration the entire measured range. We believe that this method of evaluating the internal diffusion coefficients from kinetic measurements gives reliable results and — moreover — is of a general significance<sup>1,7</sup>.

### THEORETICAL

The characteristics of the studied system are following: adsorbent granules have the form of a finite cylinder of radius  $R$  and length  $L$ ; the time dependence of the radius  $R$ , at a constant  $R/L$ , indicates that the system can be phenomenologically described by equations (2) and (3) which acquire for this geometry of granules the following form

$$\frac{\partial c}{\partial t} = D_e \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \right), \quad (5)$$

where  $r$  and  $z$  are cylindrical coordinates whose origin lies in the center of the cylinder, and  $D_e$  is given by

$$D_e = \frac{D}{1 + K}, \quad (6)$$

$K$  is the slope of the isotherm linearized over the given region.

Towards the surface of the particle (which is either empty or uniformly saturated) a rectangular concentration profile was introduced at the time  $t = 0$ . These conditions correspond to the following initial and boundary conditions:

$$c(R, z, t) = \begin{cases} 0 & \text{for } t < 0 \\ C_1 & \text{for } t \geq 0 \end{cases} \quad c(r, \pm L/2, t) = \begin{cases} 0 & \text{for } t < 0 \\ C_1 & \text{for } t \geq 0 \end{cases} \quad (7)$$

$$c(r, z, 0) = C_0 \text{ for } 0 < r < R \text{ and } -1/2L < z < 1/2L.$$

Because of symmetrical properties of the particle, it holds

$$\frac{\partial c(0, z, t)}{\partial r} = 0; \quad \frac{\partial c(r, 0, t)}{\partial z} = 0. \quad (8)$$

Solution of this set of equations is given, *e.g.*, in ref.<sup>2</sup>; from this solution the expression for saturation is derived:

$$\gamma = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 (2m-1)^2} \exp \left[ - \left( \mu_n^2 + \frac{(2m-1)^2 \pi^2}{K^2} \right) \tau \right] \quad (9)$$

where  $\mu_n$  is the  $n$ -th root of the first kind Bessel function of the  $n$ -th order of the complex argument  $z$ , and  $\tau$  is a dimensionless parameter defined by

$$\tau = D_e t / R^2. \quad (10)$$

With the use of equation (4) one obtains from (10)

$$f = D_e / R^2. \quad (11)$$

The function  $\gamma - \tau$  can be regarded as a distribution function of a random quantity  $\bar{\tau}$  which gives a probability that a value of a quantity  $\bar{\tau}$  is smaller than  $\tau$ . Therefore, one can write that  $\gamma(\tau) = P(\bar{\tau} \leq \tau)$ . From this point of view,  $\gamma(\tau)$  can be regarded as a probability that a sorbent molecule passes through the particle surface during the time  $\bar{\tau} < \tau$ . The derivative  $d\gamma/d\tau$  is the probability density  $p(\tau)$ . Statistics then gives the expression for the mean value  $\bar{\tau}^*$  of the random quantity  $\bar{\tau}$ :

$$\bar{\tau}^* = \int_{-\infty}^{+\infty} \tau p(\tau) d\tau. \quad (12)$$

As in our case  $p(\tau)$  differs from zero only for  $\tau \geq 0$ , equation (12) can be written as

$$\bar{\tau}^* = \int_0^{+\infty} \tau p(\tau) d\tau. \quad (13)$$

It is evident that this mean value  $\bar{\tau}^*$  is equal – in our case – to the area limited by the function  $\gamma - \tau$ , by the abscissa axis, and by the line  $\gamma = 1$ ; therefore, it can be evaluated from

$$\bar{\tau}^* = \int_0^1 \tau d\gamma = \int_0^{\infty} (1 - \gamma) d\tau. \quad (14)$$

Equation (14) can be used to calculate  $\bar{\tau}^*$  for various shapes of the kinetic curves, either by substituting the analytic solution of the diffusion problem for a given shape of the adsorbent particle and a given type of the initial and boundary conditions,

or by a numerical solution<sup>7</sup>. For a cylinder of various ratios  $L/R = A$ , the following expression was obtained by substituting (9) into (14):

$$\bar{\tau}^* = \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \left[ \mu_n^2 (2m-1)^2 + \frac{\mu_n^2 (2m-1)^2 \pi^2}{A^2} \right]^{-1}. \quad (15)$$

For the ratios  $L/R = 2, 4, \infty$  the values of  $\bar{\tau}^* 0.07506, 0.0995, \text{ and } 1/8$  were obtained, respectively. Using equation (10) or (11) for the mean value  $\bar{\tau}^*$  and  $\bar{i}^*$  of the quantity  $\bar{\tau}$  or  $\bar{i}$ , one obtains the following relation that can be used to calculate the diffusion coefficient  $D_c$ :

$$f = D_c/R^2 = \bar{\tau}^*/\bar{i}^*. \quad (16)$$

## EXPERIMENTAL

### Apparatus

Kinetic curves were measured using an vacuum apparatus schematically shown in Fig. 1. The apparatus was pumped down to pressures of  $10^{-5}$  Torr by a rough pump and a mercury diffusion pump. Adsorbent granules 1 were placed into a coil made of a fine tungsten wire and suspended by the quartz spiral 2. Extension of the spiral as well as readings of the mercury manometer 3 used to measure benzene pressure were determined by means of the cathetometer KM-8. The glass joint 4 was covered with mercury. Separation of the adsorption region from the vacuum line was achieved by means of the mercury valve 5 so that the apparatus volume could not come in contact with vacuum grease. Adsorption region was separated from the sorbate reservoir by the mercury valve 6 constructed in such a way that it would not lower the line diameter and would not limit the transport of sorbate molecules. The necessary benzene vapour pressure was obtained by thermostating the reservoir 7. The 10 l side volume 8 was added to the reservoir to ensure a constant vapour pressure of the adsorbate namely during the early stages of the kinetic measurements.

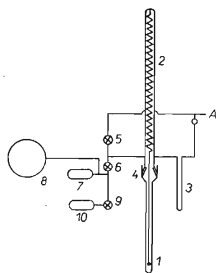


FIG. 1

Schematics of the Vacuum Apparatus used in Measurements of Adsorption Kinetics

Explanation see text.

Cylindrical sorbent particles of the ratio  $L/R = 4$  were chosen for the experiments. Prior to the measurements, the samples were heated at  $350^\circ\text{C}$  until their weight did not change. During the measurements, samples were kept at a constant temperature  $20 \pm 0.05^\circ\text{C}$ . The sensitivity of the quartz spiral was  $1.16 \text{ mg/mm}$ . Extension of the spiral was determined with an accuracy of  $\pm 0.01 \text{ mm}$ . Samples weight varied between 10 and 40 mg.

#### Compounds Used

Benzene of analytical purity used as the sorbate, was dried and distilled in a forty-stage plate column. Its vapour pressure was measured in the vacuum apparatus and found to be in agreement with the published values for pure benzene. Prior to the experiment, benzene was dried within the apparatus in the additional reservoir, distilled (*in vacuo*) into another ampule, and subjected to a multiple process of freezing the substance, pumping away the gaseous phase, and melting it. In this way noble gases contained in the liquid sorbate were removed (according to our experience, noble gases decrease the rate of adsorption).

Active charcoal SK was used as the adsorbent. This specimen was used because it was activated by inorganic salts (potassium sulphide), and this method is regarded as a homogeneous activation. Adsorption equilibrium of benzene can be described at  $20^\circ\text{C}$  and over the pressure range  $1 \cdot 10^{-5}$  to  $1 \cdot 10^{-1}$  Torr by the Dubinin equation<sup>2</sup> for charcoal of the first structural type using the following values of the constants:  $W_0 = 0.557 \text{ cm}^3/\text{g}$ , and  $B = 0.802 \cdot 10^6$ .

#### RESULTS AND DISCUSSION

Using the above mentioned procedure, the kinetic curves of benzene vapours were measured at  $20^\circ\text{C}$  for three pressure differences:  $\Delta p_1 = p_1 = 0.29 \text{ Torr}$ ;  $\Delta p_2 = p_2 - p_1 = 0.47 \text{ Torr}$ ;  $\Delta p_3 = p_3 - p_2 = 1.30 \text{ Torr}$ . From the experimental curves the quantities  $\bar{t}^*$  were evaluated using the Simpson's rule, and the curves were transformed by means of the factor  $f$  (see equation (16)) into the  $\gamma - \tau$  coordinates. The values obtained are given in Fig. 2 and Fig. 3.

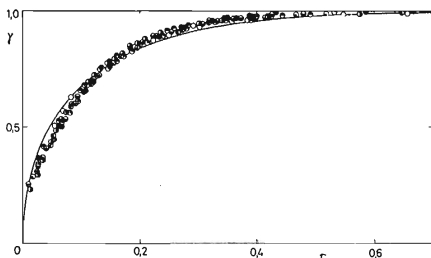


FIG. 2

Experimental Data of the Kinetic Measurements in  $\gamma - \tau$  Coordinates for the Pressure Difference  $\Delta p_1$

Solid curve calculated by Eq. (9)

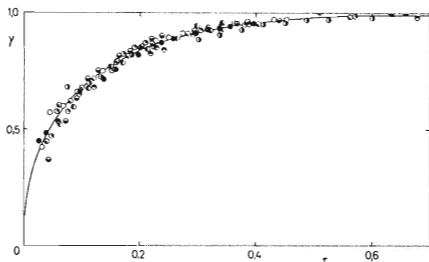


FIG. 3

Experimental Data of the Kinetic Measurements in  $\gamma$ - $\tau$  Coordinates for the Pressure Difference  $\Delta p_2$  (○ ● ◐ ◑ ◒ ◓) and  $\Delta p_3$  (⊙ ⊚)

Solid curve calculated by Eq. (9)

Comparison of the experimental points with the theoretical curve shows that experiments carried out at pressure differences  $\Delta p_2$  and  $\Delta p_3$  are in a good agreement with the theoretical curve (Fig. 3), while a systematic deviation can be seen in kinetic curves for  $\Delta p_1$  (Fig. 2). Evidently, the reason for this systematic deviation is that in the pressure range in question the adsorption isotherm deviates from the straight line cutting through the particular interval, while for higher pressure differences a similar cut represents a good approximation of the adsorption isotherm.

A larger scatter of points in Fig. 3 is due to the fact that the tangent of the adsorption isotherm is considerably smaller than in the case of the first pressure difference. Consequently, absolute increase of the weight of the adsorbent particle is smaller, while the time dependence is steeper. As a result, the experimental error is larger. This fact together with the fact that the isotherm is linear over the given range lead us to an attempt to show the applicability and usefulness of using the entire course of the kinetic curve to calculate the effective coefficient of internal diffusion  $D_e$  by means of  $\bar{t}^*$ . The mean value of  $D_e$  as evaluated with the use of equation (16) from the kinetic curves of the  $\Delta p_2$  group is  $D_e = 9.88 \cdot 10^{-6} \text{ cm}^2/\text{s}$ .

It follows from Fig. 2 that the deviation of experimental points from the theoretical curve (corresponding to the linear case) is so large that the reported values cannot be used to calculate the coefficient of internal diffusion  $D_e$ . It will be shown in our forthcoming paper that the value of  $\bar{t}^*$  is always smaller in the case of a convex isotherm than in the case of a linear one.

*Technical help of Mrs E. Bendová is gratefully acknowledged.*

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Translated by Z. Herman.