

# Kinetics and dynamics of gas and vapour adsorption on solid sorbents. V.

## Verification of the equations of adsorption dynamics in fixed bed at variable mass-transfer coefficient and at negligible influence of longitudinal diffusion

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The validity of the equations of adsorption dynamics in fixed bed derived on the assumption of variable resistance to the mass transfer in solid phase has been verified. These equations enable us to correlate precisely the experimental data. Evaluation of the dependence of the coefficients  $k_{ov}$  and  $K$  on the granularity of sorbent and the gas velocity showed that the physical assumptions used for the formulation of the equations of adsorption dynamics at variable solid phase resistance are correct.

In the preceding paper [1] the equations of adsorption dynamics in fixed bed under constant-pattern conditions were expressed for variable overall mass-transfer coefficient and negligible longitudinal diffusion on condition that the adsorption equilibria might be described by the Langmuir equation of adsorption isotherm. Since the mass-transfer rate is affected by the resistance in gaseous and solid phase, the dimensionless time necessary for the change of the relative concentration at a given height from  $Q$  to  $(1 - Q)$  may be expressed by equation

$$\Delta Z = \left( \frac{2}{\Theta_0} - K - 1 \right) \ln \frac{1 - Q}{Q} + K \Theta_0 (1 - 2Q). \quad (1)$$

This equation can be transformed into the form:

$$\Delta Z = (1 - K) \Delta Z_g + K \Delta Z_s, \quad (2)$$

where

$$\Delta Z_g = \frac{2 - \Theta_0}{\Theta_0} \ln \frac{1 - Q}{Q} \quad (3)$$

and

$$\Delta Z_s = \frac{2(1 - \Theta_0)}{\Theta_0} \ln \frac{1 - Q}{Q} + \Theta_0 (1 - 2Q). \quad (4)$$

The relationship between the dimensionless time  $\Delta Z$  and the real period  $\Delta t$  during which the relative concentration changes from  $Q$  to  $(1 - Q)$  is given by the expression

$$\Delta Z = \frac{k_{ov}}{U_{ov}} \Delta t. \quad (5)$$

The equation (3), which agrees with the *Bikson* [2] equation has been derived on the assumption that the resistance in solid phase does not influence the mass-transfer rate. The same relationship may be obtained assuming that the mass-transfer rate is affected by the resistance in both phases and the overall mass-transfer coefficient is constant. In equation (4) only the effect of the solid phase resistance is taken into consideration.

Because of the complexity and heterogeneity of the system the equations are of semi-empirical character. By the analysis of extensive experimental material it has, however, been found that these equations express precisely the dynamics of vapour adsorption on active charcoal within the experimental conditions. In this paper the validity of these equations is tested.

### Experimental

To verify the validity of equations (1–5) the results of the measurements of dynamics of the benzene vapour adsorption on active charcoal presented by *Zikánová* [3] were used. Originally it was not the aim of these measurements to prove the validity of the above equations which were derived later.

Table 1

Dubinin and Langmuir constants for the samples of activated carbon used

| Sample of activated carbon | Dubinin isotherm                            |   |                              | Langmuir isotherm                            |   |                              |
|----------------------------|---|---|------------------------------|--|---|------------------------------|
|                            | $W_0$<br>[cm <sup>3</sup> g <sup>-1</sup> ] | $B \cdot 10^{-6}$<br>[K <sup>-2</sup> ] | Range of validity<br>$p/p_s$ | $a_m \cdot 10^{-5}$<br>[g cm <sup>-3</sup> ] | $b \cdot 10^{-6}$<br>[cm <sup>3</sup> g <sup>-1</sup> ] | Range of validity<br>$p/p_s$ |
| KAH                        | 0.397                                       | 1.00                                    | 0.001–0.1                    | 2.530  | 0.82  | 0.01–0.3                     |
| SK                         | 0.570                                       | 0.85                                    | 0.001–0.1                    | 2.990  | 0.77  | 0.01–0.3                     |
| 27                         | 0.273                                       | 0.49                                    | 10 <sup>-5</sup> –0.1        | 1.862  | 3.26  | 0.01–0.3                     |
| 29                         | 0.388                                       | 0.68                                    | 10 <sup>-5</sup> –0.1        | 3.342  | 1.37  | 0.01–0.3                     |
| 31                         | 0.425                                       | 0.79                                    | 10 <sup>-5</sup> –0.1        | 2.130  | 0.94  | 0.01–0.3                     |
| 33                         | 0.566                                       | 0.90                                    | 10 <sup>-5</sup> –0.1        | 2.082  | 0.60  | 0.01–0.3                     |

Table 2

Structural characteristics of the samples of activated carbon used

| Sample of activated carbon | $V_s$<br>[cm <sup>3</sup> /cm <sup>3</sup> ] | $V_{mi}$<br>[cm <sup>3</sup> /cm <sup>3</sup> ] | $V_t$<br>[cm <sup>3</sup> /cm <sup>3</sup> ] | $V_i$<br>[cm <sup>3</sup> /cm <sup>3</sup> ] | $S_i$<br>[m <sup>2</sup> g <sup>-1</sup> ] | $Q_v$<br>[g cm <sup>-3</sup> ] | $Q_{He}$<br>[g cm <sup>-3</sup> ] | $Q_{Fg}$<br>[g cm <sup>-3</sup> ] |
|----------------------------|--|---|--|--|--|--------------------------------|-----------------------------------|-----------------------------------|
| KAH                        | 0.633  | 0.293   | 0.340  | —  | —  | 0.455                          | 2.09                              | 0.768                             |
| SK                         | 0.742  | 0.331   | 0.411  | 0.165  | —  | 0.376                          | 2.42                              | 0.626                             |
| 27                         | 0.586  | 0.223   | 0.363  | 0.086  | 49   | 0.530                          | 2.13                              | 0.880                             |
| 29                         | 0.678  | 0.238   | 0.440  | 0.115  | 63   | 0.415                          | 2.13                              | 0.685                             |
| 31                         | 0.734  | 0.211   | 0.523  | 0.147  | 68   | 0.337                          | 2.13                              | 0.567                             |
| 33                         | 0.803  | 0.200   | 0.603  | 0.215  | 82   | 0.233                          | 2.13                              | 0.419                             |

Zikánová measured the dynamics of adsorption on six kinds of activated carbon. The samples denoted KAH and SK were activated with zinc chloride whereas the samples denoted 27, 29, 31, and 33 were activated with water vapour. The characteristic values of Dubinin and Langmuir constants of the used sorbents calculated from the adsorption isotherms of benzene at 20°C are presented in Table 1. Table 2 contains the structural characteristics of these carbons. It follows from Tables 1 and 2 that the kinds of activated carbon used differed considerably in structure which enabled us to test the validity of equation (1) on different types of adsorbents. The experiments were performed at different gas velocities with the sorbents of varying granularity at 20°C and at the concentration of benzene in gaseous mixture  $C_0 = 18 \text{ g m}^{-3}$ . The bed height was 4.4 cm. Constant-pattern conditions were observed in the whole range of working conditions.

The course of break-through curves behind the adsorbent bed was determined. From the break-through curve the period of time  $\Delta t_{\text{exp}}$ , during which the relative concentration of adsorbate in gas behind the bed changed from  $Q$  to  $(1 - Q)$ , was determined for each  $Q$ .

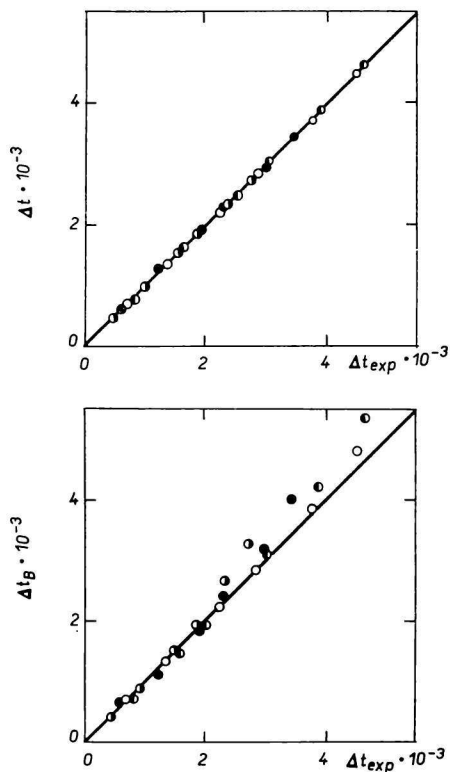


Fig. 1. Comparison of the experimental values  $\Delta t_{\text{exp}}$  with the values  $\Delta t$  and  $\Delta t_B$  calculated according to equations (1) and (3), respectively; experiments 4, 7, 11, and 12.

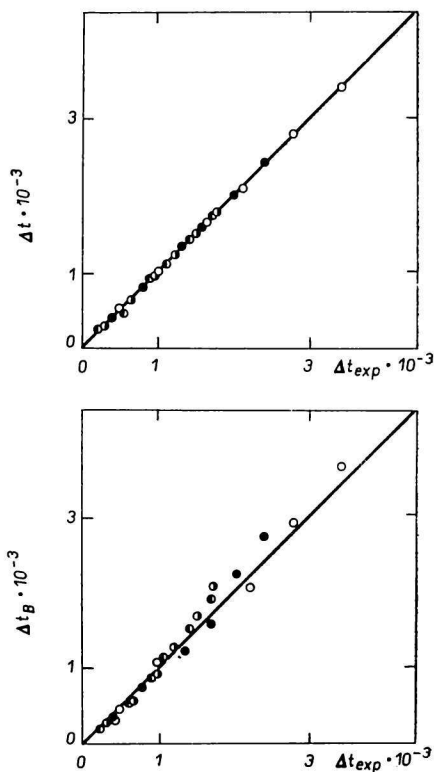


Fig. 2. Comparison of the experimental values  $\Delta t_{\text{exp}}$  with the values  $\Delta t$  and  $\Delta t_B$  calculated according to equations (1) and (3), respectively; experiments 5, 8, 9, and 13.

In order to verify the Bikson equation (3), Zikánová expressed the variation of  $\Delta t_{\text{exp}}$  with  $[(2 - \Theta_0)/\Theta_0] \ln [(1 - Q)/Q]$  for individual experiments. The character of this relationship has not been a straight line what confirms that equation (3) does not describe the adsorption dynamics in the investigated systems. Thus the assumption that the overall mass-transfer coefficient is constant in the investigated systems is oversimplified and for this reason its dependence on the relative concentration  $Q$  must be assumed.

To verify the validity of equation (1), it was transformed into the linearized form:

$$\frac{\Delta t}{\Delta Z_g} = \frac{k_{0v}}{\Gamma_{0v}} (1 - K) + \frac{k_{0v}}{\Gamma_{0v}} K \frac{\Delta Z_s}{\Delta Z_g} \quad (6)$$

The values  $\Theta_0$  and  $\Gamma_{0v}$  were calculated from the equation of adsorption isotherm. Using equations (3, 4) the expressions  $\frac{\Delta t_{\text{exp}}}{\Delta Z_g}$  and  $\frac{\Delta Z_g}{\Delta Z_s}$  were calculated for each pair of  $Q$  and  $\Delta t_{\text{exp}}$  and from the relationship between  $\frac{\Delta t_{\text{exp}}}{\Delta Z_g}$  and  $\frac{\Delta Z_s}{\Delta Z_g}$  the values  $k_{0v}$  and  $K$  were determined by the method of least squares. By using these results the value  $\Delta t_{\text{calc}}$  was then calculated from relationships (1) and (5) for each  $Q$ . In an analogous way the experimental material was evaluated according to the Bikson equation (3).

### Discussion

The results of the evaluation of all 37 experiments are given in paper [4]. It has been confirmed for all experiments that equation (1) expresses precisely the adsorption dy-

Table 3

Comparison of the values  $\Delta t$  and  $\Delta t_B$  calculated according to equations (1) and (3) respectively with the experimental values  $\Delta t_{\text{exp}}$  for  $Q = 0.027$

| Experiment                          | $\Delta$ (%) | $\Delta_B$ (%) |       | Experiment | $\Delta$ (%) | $\Delta_B$ (%) |       |
|-------------------------------------|--------------|----------------|-------|------------|--------------|----------------|-------|
| 1                                   | + 1.10       | + 10.20        | 0.993 | 20         | + 1.58       | + 7.10         | 0.991 |
| 2                                   | + 0.97       | + 11.07        | 0.993 | 21         | + 0.12       | + 23.54        | 0.971 |
| 3                                   | + 0.58       | + 11.33        | 0.991 | 22         | + 1.50       | + 19.02        | 0.938 |
| 4                                   | + 0.76       | + 7.40         | 0.997 | 23         | + 0.75       | + 22.50        | 0.987 |
| 5                                   | + 0.38       | + 5.09         | 0.999 | 24         | + 0.64       | + 13.97        | 0.997 |
| 6                                   | + 0.13       | + 17.60        | 0.998 | 25         | + 0.49       | + 5.90         | 0.998 |
| 7                                   | + 0.73       | + 18.57        | 0.987 | 26         | + 2.52       | + 24.50        | 0.999 |
| 8                                   | + 1.42       | + 15.08        | 0.949 | 27         | - 0.21       | + 19.55        | 0.991 |
| 9                                   | + 0.53       | + 13.27        | 0.998 | 28         | + 0.62       | + 17.29        | 0.990 |
| 10                                  | + 2.20       | + 9.64         | 0.980 | 29         | 0.00         | + 11.87        | 0.997 |
| 11                                  | - 0.10       | + 16.13        | 0.997 | 30         | + 1.64       | + 14.16        | 0.994 |
| 12                                  | + 0.22       | + 19.60        | 0.998 | 31         | + 0.88       | + 18.05        | 0.994 |
| 13                                  | + 0.62       | + 17.63        | 0.993 | 32         | + 1.20       | + 5.24         | 0.995 |
| 14                                  | - 0.64       | + 12.90        | 0.988 | 33         | + 3.35       | 10.02          | 0.972 |
| 15                                  | + 0.85       | + 4.79         | 0.994 | 34         | - 0.76       | + 5.73         | 0.995 |
| 16                                  | - 0.43       | + 14.18        | 0.978 | 35         | + 0.11       | + 13.90        | 0.993 |
| 17                                  | + 0.48       | + 10.62        | 0.998 | 36         | + 0.58       | + 3.78         | 0.995 |
| 18                                  | - 0.38       | + 10.91        | 0.993 | 37         | -            | -              | 0.992 |
| 19                                  | + 0.71       | + 10.24        | 0.997 | -          | -            | -              | -     |
| Arithmetic mean for all experiments |              |                |       |            | 0.84         | 11.86          | 0.989 |

Table 4

Values of  $k_{0v}$  and  $K$  for activated carbon KAH

| KAH                         | $w$<br>[cm s <sup>-1</sup> ] | $d$ [cm]  |           |  |  |  |
|-----------------------------|------------------------------|-----------|-----------|--|--|--|
|                             |                              | 0.15–0.20 | 0.10–0.12 | $6.0 \times 10^{-2}$<br>$7.5 \times 10^{-2}$ | $3.0 \times 10^{-2}$<br>$4.2 \times 10^{-2}$ | $1.5 \times 10^{-2}$<br>$2.0 \times 10^{-2}$ |
| $k_{0v}$ [s <sup>-1</sup> ] | 1.77                         | 1.946     | 2.572     | 3.275  | 4.710  | 6.819  |
|                             | 5.17                         | 2.797     | 4.260     | 6.839  | 10.028                                       | 16.937                                       |
|                             | 8.17                         | 3.424     | 5.249     | 8.318  | 11.495                                       | 24.170                                       |
| $K$                         | 1.77                         | 0.561     | 0.573     | 0.595  | 0.470  | 0.381  |
|                             | 5.17                         | 0.876     | 0.794     | 0.698  | 0.669  | 0.321  |
|                             | 8.17                         | 0.746     | 0.805     | 0.787  | 0.769  | 0.246  |

Table 5

Values of  $k_{0v}$  and  $K$  for activated carbon SK

| SK                          | $w$<br>[cm s <sup>-1</sup> ] | $d$ [cm]  |           |  |  |  |
|-----------------------------|------------------------------|-----------|-----------|--|--|--|
|                             |                              | 0.15–0.20 | 0.10–0.12 | $6.0 \times 10^{-2}$<br>$7.5 \times 10^{-2}$ | $3.0 \times 10^{-2}$<br>$4.2 \times 10^{-2}$ | $1.5 \times 10^{-2}$<br>$2.0 \times 10^{-2}$ |
| $k_{0v}$ [s <sup>-1</sup> ] | 1.77                         | 1.753     | 2.647     | 5.329  | 4.932  | 7.362  |
|                             | 8.17                         | 3.008     | 5.350     | 7.557  | 12.470                                       | 22.160                                       |
|                             | 18.00                        | —         | 7.221     | 12.180                                       | 18.510                                       | 24.090                                       |
| $K$                         | 1.77                         | 0.690     | 0.523     | 0.601  | 0.417  | 0.380  |
|                             | 8.17                         | 0.890     | 0.808     | 0.868  | 0.681  | 0.353  |
|                             | 18.00                        | —         | 0.880     | 0.817  | 0.754  | 0.558  |

Table 6

Values of  $k_{0v}$  and  $K$  for activated carbon 27, 29, 31, and 33

| $d$ [cm]<br>0.15–0.20       | $w$<br>[cm s <sup>-1</sup> ] | Sample of activated carbon |       |       |       |
|-----------------------------|------------------------------|----------------------------|-------|-------|-------|
|                             |                              | 27                         | 29    | 31    | 33    |
| $k_{0v}$ [s <sup>-1</sup> ] | 1.77                         | 2.654                      | 3.323 | 3.016 | 4.412 |
|                             | 8.17                         | 4.628                      | 8.130 | 8.024 | —     |
| $K$                         | 1.77                         | 0.493                      | 0.358 | 0.583 | 0.234 |
|                             | 8.17                         | 0.691                      | 0.395 | 0.634 | —     |

namics of benzene vapour on different kinds of activated carbon. Because of the large extent of material it is not possible to present all results in this paper. Figs. 1 and 2 show the correlation of  $\Delta t_{\text{exp}}$  with  $\Delta t$  calculated from equation (1) as well as the correlation of  $\Delta t_{\text{exp}}$  with  $\Delta t_{\text{B}}$  calculated from the Bikson equation (3) for 8 experiments. While all the points calculated from equation (1) are practically on a straight line, the use of Bikson equation results in a considerable straggling of points especially in the region of low concentrations of adsorbate. This region is the most important for practice.

The precision with which equation (1) describes the adsorption dynamics is manifested by the percent deviations of the values  $\Delta t$  calculated according to equation (1) from the values  $\Delta t_{\text{exp}}$  determined experimentally. These deviations are in Table 3 denoted by the symbol  $\Delta$  (%). They refer to the lowest value  $Q = 2.7 \times 10^{-2}$  for all 37 experiments. The arithmetic mean of these deviations is 0.84% which confirms the high precision of that mode of expression. For all experiments this value refers to the lowest concentration at which the deviations are largest when compared with those obtained at higher concentrations. Table 3 contains also the percent deviations of the values  $\Delta t_B$  calculated according to equation (3) from the values  $\Delta t_{\text{exp}}$  which are denoted by the symbol  $\Delta_B$  (%). The arithmetic mean of these deviations is 11.86% for all experiments in contrast to the value 0.84% obtained if equation (1) is used.

The high precision achieved by employing equation (1) is confirmed also by the correlation coefficient for  $\Delta t$  and  $\Delta t_{\text{exp}}$  the average value of which is 0.989 for all experiments.

Besides the determination of the precision with which equation (1) expresses the adsorption dynamics, it is necessary to find out the dependence of the coefficients  $k_{0v}$  and  $K$  on experimental conditions. Tables 4–6 show the values of these coefficients together with the corresponding data about working conditions.

Comparison of the coefficients  $K$  given for individual experiments in Tables 4–6 shows that their values vary in the range from 0 to 1 as postulated by physical justification of this quantity analyzed in paper [1].

The value of  $K$  decreases with decreasing granularity of sorbent which also involves the decrease in the influence of the solid phase resistance. The value of  $K$  increases with increasing gas velocity because the effect of external diffusion on the overall rate of process decreases. Some fluctuations in above relations are due to various factors, e.g. heterogeneity of bed. But the above-mentioned conclusions ensue unambiguously from the comparison of the values of  $K$ . In this way the accuracy of physical assumptions involved in the derivation of equation (1) has been proved as well.

### Symbols

|                 |   |
|-----------------|---|
| $a_m$           | adsorption capacity of monomolecular layer ( $\text{g cm}^{-3}$ )   |
| $a_{0v}^*$      | equilibrium adsorption capacity corresponding to $C_0$ and referred to a volume unit of bed ( $\text{g cm}^{-3}$ )  |
| $B$             | constant in the Dubinin equation of adsorption isotherm ( $\text{K}^{-2}$ )   |
| $b$             | constant in the Langmuir equation of adsorption isotherm ( $\text{cm}^3 \text{g}^{-1}$ )                            |
| $C$             | concentration of adsorbate in gas ( $\text{g cm}^{-3}$ )  |
| $C_0$           | concentration of adsorbate in gas entering the column ( $\text{g cm}^{-3}$ )  |
| $d$             | diameter of granules of adsorbent (cm)  |
| $K$             | coefficient characterizing the contribution of resistance in solid phase to the overall resistance to mass transfer |
| $k_{0v}$        | characteristic value of the overall mass-transfer coefficient referred to a volume unit of bed ( $\text{s}^{-1}$ )  |
| $p$             | partial pressure of adsorbate in gas (torr)   |
| $p_s$           | pressure of the saturated vapour of adsorbate (torr)  |
| $Q$             | relative concentration of adsorbate in gas  |
| $r_c$           | correlation coefficient   |
| $S_i$           | surface of intermediate pores ( $\text{m}^2 \text{g}^{-1}$ )  |
| $V_{\text{ml}}$ | volume of micropores ( $\text{cm}^3/\text{cm}^3$ )  |

|                         |  |
|-------------------------|--|
| $V_i$                   | volume of intermediate pores ( $\text{cm}^3/\text{cm}^3$ )   |
| $V_s$                   | total volume of pores ( $\text{cm}^3/\text{cm}^3$ )  |
| $V_t$                   | volume of transport pores ( $\text{cm}^3/\text{cm}^3$ )  |
| $W_0$                   | adsorption volume ( $\text{cm}^3 \text{g}^{-1}$ )  |
| $w$                     | linear gas velocity based on empty column cross section ( $\text{cm s}^{-1}$ )   |
| $\Gamma_{0v}$           | ratio $a_{0v}^*/C_0$   |
| $\Delta$ (%)            | $\frac{\Delta t - \Delta t_{\text{exp}}}{\Delta t_{\text{exp}}}$   |
| $\Delta_B$ (%)          | $\frac{\Delta t_B - \Delta t_{\text{exp}}}{\Delta t_{\text{exp}}}$   |
| $\Delta t$              | period of time during which the relative concentration changes from $Q$ to $(1 - Q)$ under constant-pattern conditions; calculated according to equation (1) (s) |
| $\Delta t_{\text{exp}}$ | period of time during which the relative concentration changes from $Q$ to $(1 - Q)$ under constant-pattern conditions; found experimentally (s)                 |
| $\Delta t_B$            | period of time during which the relative concentration changes from $Q$ to $(1 - Q)$ under constant-pattern conditions; calculated according to equation (3) (s) |
| $\Delta Z$              | dimensionless time for the range from $Q$ to $(1 - Q)$ calculated according to equation (1)  |
| $\Delta Z_g$            | dimensionless time for the range from $Q$ to $(1 - Q)$ calculated according to equation (3)  |
| $\Delta Z_s$            | dimensionless time for the range from $Q$ to $(1 - Q)$ calculated according to equation (4)  |
| $\Theta_0$              | equilibrium degree of the covering of active surface at $C_0$  |
| $\rho_{\text{He}}$      | helium density of adsorbent ( $\text{g cm}^{-3}$ )   |
| $\rho_{\text{Hg}}$      | mercury density of adsorbent ( $\text{g cm}^{-3}$ )  |
| $\rho_v$                | bulk density of adsorbent ( $\text{g cm}^{-3}$ )   |

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