The kinetics of the adsorption of a mixture of two substances (1 and 2) from a flux, when the limiting step of the process is external mass exchange, will be discussed. In contrast to [1], it is suggested that adsorption occurs not on a pure adsorbent, but on an adsorbent preliminarily saturated with component 2.

1. Let us consider that in the flux the concentrations of substances 1 and 2 are \( c_1 \) and \( c_2 \), and the adsorbent was preliminarily saturated with substance 2 at a concentration \( c_2^0 \). Then the problem under investigation is described [1] by the following equations and conditions:

\[
\frac{d\alpha_1}{dt} = \beta_1 [c_1 - \varphi_1 (\alpha_1, \alpha_2)], \quad \frac{d\alpha_2}{dt} = \beta_2 [c_2 - \varphi_2 (\alpha_1, \alpha_2)]
\]

with the initial conditions

\[
\alpha_1 (0) = 0, \quad \alpha_2 (0) = \alpha_2 (0, c_2^0)
\]

Here \( \alpha_1 \) represents the average concentrations of the substances over the grain in the "stationary," adsorption phase; \( c_i = \varphi_i (\alpha_1, \alpha_2) (\alpha_1 = \alpha_i (c_1, c_2)) \), \( i = 1, 2 \) represents the equations of the adsorption isotherms of the mixture; \( \beta_1 \) and \( \beta_2 \) are the coefficients of external mass exchange.

When \( t \to \infty \), the concentrations \( \alpha_i \) should approach the equilibrium values \( \alpha_i^0 = \alpha_i (c_1^0, c_2^0) \).

After the introduction of dimensionless variables

\[
\theta_i = \frac{a_i}{a_i^0}, \quad \tau = \frac{tc_i^0}{a_i^0}, \quad \varphi_i^* (\theta_1, \theta_2) = \varphi_i (\alpha_1, \alpha_2), \quad \mu = \frac{c_2^0 a_1^0 \varphi_1^0}{c_1^0 a_2^0 \varphi_2^0}
\]

Eqs. (1.1) can be represented as

\[
\frac{d\theta_1}{d\tau} = 1 - \varphi_1^* (\theta_1, \theta_2), \quad \frac{d\theta_2}{d\tau} = \mu [1 - \varphi_2^* (\theta_1, \theta_2)]
\]

with the initial conditions

\[
\theta_1 (0) = 0, \quad \theta_2 (0) = \frac{a_2 (0)}{a_2^0} = \theta_2 (0, c_2^0) = A, \quad 0 \leq \theta_1 \leq 1, \quad \theta_2 (\infty) = 1
\]

Division of the second equation of (1.3) by the first also gives

\[
\frac{d\theta_2}{d\theta_1} = \frac{1 - \varphi_1^* (\theta_1, \theta_2)}{1 - \varphi_2^* (\theta_1, \theta_2)}, \quad \theta_2 (0) = A, \quad (\theta_1 (1) = 1)
\]

From a thermodynamic analysis [2, 3] it follows that

\[
\frac{\partial f_1}{\partial c_2} < 0, \quad \frac{\partial f_2}{\partial c_1} < 0 \tag{1.5a}
\]

or

\[
\frac{\partial f_1}{\partial c_2} > 0, \quad \frac{\partial f_2}{\partial c_1} > 0 \tag{1.5b}
\]

The case (1.5b) was observed experimentally in [4]. In most cases, however, the inequalities (1.5a) are fulfilled (the adsorption of one component is reduced in the presence of the other).
Let us limit ourselves subsequently to a consideration of the case (1.5a) and let us investigate for the sake of definition the Langmuir-like adsorption isotherms of the mixtures

$$a_1 = \frac{a_1 a_2 b_1 c_1}{1 + b_1 c_1 + b_2 c_2}, \quad a_2 = \frac{a_2 a_3 b_2 c_2}{1 + b_1 c_1 + b_2 c_2}.$$  

(1.6)

Then instead of (1.4) we have

$$\frac{d\theta_2}{d\theta_1} = \mu \frac{\tau_1 (1 - \theta_2) + (1 + \tau_2)(1 - \theta_1)}{(1 + \tau_1)(1 - \theta_1) + \tau_2 (1 - \theta_3)},$$

$$\tau_2 (0) = 1 + \frac{\tau_1}{1 + \tau_2} = A > 1$$

$$0 \leq \theta_1 \leq 1, \quad 1 \leq \theta_2 \leq A$$

$$\tau_1 = b_1 c_1^a, \quad \mu = \frac{a_2 a_3 b_1}{a_2 a_3 b_2}$$

(1.7)

It is not difficult to see that at the point \((\theta_1 = 0, \quad \theta_2 = A)\) \(d\theta_2/d\theta_1 = 0\), \(d^2\theta_2/d\theta_1^2 = -\mu \gamma_1 (1 + \gamma_2)/(1 + \gamma_1 + \gamma_2) < 0\). Therefore, in the region of this point the integral curve takes the form

$$\theta_2 (\theta_1) \approx 1 + \frac{\tau_1}{1 + \tau_2} - \mu \frac{\mu \tau_2 (1 + \gamma_2)}{2(1 + \gamma_1 + \gamma_2)} \theta_1^2, \quad \left( \frac{d\theta_2}{d\theta_1} \right) = 0.$$  

(1.8)

The derivative \(d\theta_2/d\theta_1\) becomes zero and infinity on the straight lines:

$$\theta_2 = \left(1 + \frac{\tau_1}{1 + \tau_2} \right) - \frac{\tau_1}{1 + \tau_2} \theta_1, \quad \theta_2 = \left(1 + \frac{\tau_1}{1 + \tau_2} \right) - \frac{1 + \tau_1}{\tau_2} \theta_1,$$

(1.9)

respectively. The indicated straight lines are denoted by the numbers 1 and 2 in Fig. 1.

The point \((1, 1)\) is singular for Eq. (1.7). A tangent to the integral curve at the same point is the following:

$$\theta_2 = 1 - B (1 - \theta_2) = (1 - B) + B\theta_1, \quad B = \left( \frac{d\theta_2}{d\theta_1} \right)_{\theta_1 = \theta_2},$$

(1.10)

where the coefficient \(B\) is determined from

$$\gamma_1 B^2 + [(1 + \gamma_1) - \mu (1 + \gamma_2)] B - \mu \gamma_1 = 0$$  

(1.11)

Since the integral curve \(\theta_2 (\theta_1)\) sought lies in the region \(0 \leq \theta_1 \leq 1\), it is easy to see that \(B < 0\) and \(\theta_2 (\theta_1)\) is included between the straight lines (1.9). In the region of the point \((0, A)\) it is approximately expressed by formula (1.8). Therefore, considering (1.11) we have finally

$$B = -\frac{[(1 + \gamma_1) - \mu (1 + \gamma_2)]}{2\gamma_2} \left[ \frac{1 + \frac{4 \mu \gamma_1 \gamma_2}{\gamma_1 \gamma_2 [(1 + \gamma_1) - \mu (1 + \gamma_2)]^2}}{1 + \frac{1 + \gamma_1}{\gamma_2}} \right],$$

$$\mu > \frac{1 + \gamma_1}{1 + \gamma_2},$$

(1.12)

$$B = -\frac{[(1 + \gamma_1) - \mu (1 + \gamma_2)]}{2\gamma_2} \left[ \frac{1 + \frac{4 \mu \gamma_1 \gamma_2}{\gamma_1 \gamma_2 [(1 + \gamma_1) - \mu (1 + \gamma_2)]^2}}{1 + \frac{1 + \gamma_1}{\gamma_2}} + 1 \right],$$

$$\mu < \frac{1 + \gamma_1}{1 + \gamma_2}.$$  

When \(\mu = (1 + \gamma_1)/(1 + \gamma_2)\) considering the aforementioned, we obtain from (1.11)

$$B = -\sqrt{\frac{\gamma_1 (1 + \gamma_1)}{\gamma_2 (1 + \gamma_2)}}$$

(1.13)

The investigated integral curve \(\theta_2 (\theta_1)\) therefore cannot have either a maximum or a minimum. On Fig. 1 this curve is depicted by the solid line 3.

Thus, in the case under consideration, in contrast to [1], a monotonic decrease in the concentration of component 2 from \(\theta_2 = A > 1\) to \(\theta_2 = 1\) is observed. At the same time, the concentration of component 1 increases from \(\theta_1 = 0\) to 1.

A solution of Eq. (1.7) can be obtained in explicit form. Actually, introducing