INVARIANT SOLUTIONS TO THE EQUATIONS OF SORPTION EQUILIBRIUM DYNAMICS AND KINETICS

L. K. Tsabek

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The theory of continuous Lie groups is used for finding invariant solutions to the equation of sorption kinetics, which describe the mass transfer in a porous symmetrical sorbent grain corresponding to a nonlinear isotherm, and invariant solutions which describe the mass transfer in a porous column with longitudinal stirring.

Invariant solutions to partial differential equations which represent specific solutions to individual problems in a small particular class, constitute one way toward obtaining various approximate solutions to problems in a larger general class. Thus, invariant solutions are widely used for solving problems in gas dynamic [1, 2], heat and mass transfer [3, 4], and other problems contiguous to those. In searching for invariant solutions we will use the theory of continuous Lie groups [5-8]. Since this is a local theory, it is not possible by its methods to find the solutions to specific problems with arbitrary boundary conditions (the groups in this case are very small and, essentially, yield trivial solutions which are of no interest). In many applications, however, the difficulties due to the nonlinearity of partial differential equations have resulted in a rather wide use of individual specific solutions for the analysis of such applications.

The sorption kinetics in symmetrical grains of a porous undeformed medium can be described by the equation of mass transfer in dimensionless variables and by the equation of the sorption isotherm:

$$\frac{\partial c^0}{\partial t}+\frac{\partial q^0}{\partial t}=\frac{\partial^2 c^0}{\partial r^2}+\frac{\nu}{r}\cdot\frac{\partial c^0}{\partial r},\quad q^0=f(c^0) \tag{1}$$

with the symmetry condition at the grain center and with the zero initial and boundary conditions:

$$\left.\frac{\partial c^0}{\partial r}\right|_{r=0}=0,\quad c^0(r,\ t)|_{r=1}=c_0(t),\quad \left.\left[c^0(r,\ t)+\varkappa\frac{\partial c^0(r,\ t)}{\partial r}\right]\right|_{r=1}=c_0(t). \tag{2}$$

Here the first boundary condition corresponds to an infinitely high rate of mass transfer and the second boundary condition corresponds to a finite rate of mass transfer at the outer grain boundary.

We note that transient nonlinear filtration of gas through porous media can be described by an equation analogous to (1) [9]. The infinitesimal operators $X = \xi(\partial/\partial t) + \eta(\partial/\partial r) + \tau(\partial/\partial c^0)$ allowable in terms of Eq. (1) will be found from the determining equation [7, 8]. In Table 1 are listed various infinitesimal operators and, for the most interesting case $1 < \nu < 2$ encountered in their applications, single-parameter subgroups of these operators. For a linear isotherm $q^0 = kc^0$ the subgroup $X_1 + \alpha X_4$ yields the solution

$c^0(r,\ t) = Ae^{\alpha t}r^{\left(\frac{1-\nu}{2}\right)}J_{\left(\frac{\nu-1}{2}\right)}(\sqrt{\alpha}r)$. By the way, this solution can be obtained by a separation of variables. The subgroup $X_2 + \alpha X_4$ yields the automorphic solution $y = (1 + k)r^2/4t$,

$$c^0(r,\ t)=At^{\left(\frac{\alpha}{2}-\frac{1+\nu}{4}\right)}e^{-y}\Phi\left(\frac{1+\nu+2\alpha}{4},\ \frac{1+\nu}{2},\ y^2\right).$$

For an arbitrary isotherm $q^0 = f(c^0)$ the operator X_2 has the automorphic solution $y = r^{-2}t$,

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$$\frac{d^2c^0}{dy^2}+\left(\frac{3-\nu}{2y}-\frac{1+\dfrac{df}{dc^0}}{4y^2}\right)\frac{dc^0}{dy}=0,\quad c^0(0)=0,\quad \left.\frac{dc^0}{dy}\right|_{y\to+\infty}=0,$$
$$c^0(y)|_{r=1}=c^0(t)=c_0(t). \tag{3}$$

This equation can be integrated numerically without difficulty, if it is reduced to an integral equation solvable by the method of successive approximations. For the isotherm $q = q_0^0(c^0)^{(1+p)} - c^0$ of the subgroup $\alpha X_1 + X_4$ we have $y = t - \alpha \ln r$, $c^0(r, t) = \exp(-2t/\alpha p)L(y)$, while the subgroup $\alpha X_2 + X_4$ yields the automorphic solution $y = r^{-\alpha}t$, $c^0(r, t) = t^{\left(\frac{\alpha-2}{\alpha p}\right)}L(y)$. For function $L(y)$ we will obtain a nonlinear ordinary differential equation, after the preceding invariant solutions have been inserted into Eq. (1). For the isotherm $q = q_0^0[\exp(bc^0) - 1] - c^0$ of the subgroup $\alpha X_1 + X_4$ we have $y = t - \alpha \ln r$, $c^0(r, t) = \exp(-2t/\alpha b)L(y)$; while the subgroup $\alpha X_2 + X_4$ yields the automorphic solution $y = r^{-\alpha}t$, $c^0(r, t) = t^{\left(\frac{\alpha-2}{\alpha b}\right)}L(y)$.

On the basis of the automorphic invariant solutions, one can reduce the nonlinear equations to a system of linear (or less nonlinear) equations with an unknown shiftable boundary (the Lame–Clapeyron–Stefan problem) by approximating a nonlinear isotherm $q^0 = f(c^0)$ with a piecewise linear (or piecewise nonlinear) function [10-12]. The validity of reducing the Stefan problem to a nonlinear parabolic equation has been discussed in [13]. For the piecewise approximation of a nonlinear isotherm

$$q(c^0)=\begin{cases} k_1c^0, & 0\leqslant c^0\leqslant c_1^*,\\ k_{i-1}c_{i-1}^*+k_ic^0, & c_{i-1}^*\leqslant c^0\leqslant c_i^*,\\ k_{n+1}c^0, & c_n^*\leqslant c^0,\ (i=2,\ 3,\ n); \end{cases} \tag{4}$$

Eq. (1) with a shiftable boundary becomes at the break points $y_i^*(t)$ on such an isotherm:

$$(1+k_i)\frac{\partial c_i^0}{\partial t}=\frac{\partial^2 c_i^0}{\partial r^2}+\frac{\nu}{r}\cdot\frac{\partial c_i^0}{\partial r},\quad y_{i-1}^*(t)\leqslant r\leqslant y_i^*(t),\quad t>0. \tag{5}$$

For the zero initial and boundary conditions (concentration continuity and concentration flow at the break points on the isotherm) we write

$$c_i^0(r,\ t)|_{t=0}=0,\quad y_i^*(t)|_{t=0}=0\quad (i=1,\ 2,\ \dots,\ n), \tag{6}$$

$$c_i^0(y_i^*(t),\ t)=c_{i+1}^0(y_i^*(t),\ t),\ \left.\left[\left(\frac{1+k_{i+1}}{1+k_i}\right)\frac{\partial c_i^0(r,\ t)}{\partial r}-\frac{\partial c_{i+1}^0(r,\ t)}{\partial r}\right]\right|_{r=y_i^*(t)}=0. \tag{7}$$

For plates which simulate grains in an undeformed medium ($\nu = 0$) [14] we find, with the aid of the subgroup $X_2 - X_5 + \alpha X_6$, the automorphic solution $y_i = \sqrt{\frac{1+k_i}{4t}}\,(1-r)$,

$$c_i^0(r,\ t)=A_i\Phi\left(\frac{1-2\alpha}{4},\ \frac{1}{2},\ -y_i^2\right)+B_iy_i\Phi\left(\frac{3-2\alpha}{4},\ \frac{3}{2},\ -y_i^2\right). \tag{8}$$

By varying the arbitrary parameter α, one can modify the function $c_0(t)$ in the boundary conditions (2). For $c_0(t) = c_0^0 = \text{const}$ ($\alpha = 1/2$) we obtain from (8)

$$c_i^0(r,\ t)=A_i+B_i\,\mathrm{erf}\,(y_i). \tag{9}$$

Taking into account conditions (2) and (6), we find

$$y_i^*(t)=1-2\alpha_i\sqrt{\frac{t}{1+k_i}}\quad(\alpha_i=\text{const}),\quad c_0^0=A_{n+1},$$
$$B_{n+1}=\frac{(c_n^*-c_0^0)}{\mathrm{erf}\,(\alpha_n\gamma_n)},$$
$$A_i=c_i^*-\frac{c_i^*-c_{i-1}^*}{\mathrm{erf}\,(\alpha_i)-\mathrm{erf}\,(\alpha_{i-1}\gamma_{i-1})},\quad B_i=\frac{c_i^*-c_{i-1}^*}{\mathrm{erf}\,(\alpha_i)-\mathrm{erf}\,(\alpha_{i-1}\gamma_{i-1})}, \tag{10}$$
$$\gamma_i=\sqrt{\frac{1+k_{i+1}}{1+k_i}}\quad(i=2,\ 3,\ \dots,\ n),\quad A_1=-B_1=\frac{c_1^*}{\mathrm{erfc}\,(\alpha_1)}.$$

TABLE 1. Infinitesimal Operators Allowable in Terms of Eq. (1)

	$f=kc^0$	$f=q_0^0 c^{0(1+p)}-c^0$	$f=q_0^0(e^{bc^0}-1)-c^0$	Arbitrary f
$\nu=0$	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}-\frac{c^0}{2}\cdot\frac{\partial}{\partial c^0}$; $X_3=t^2\frac{\partial}{\partial t}+tr\frac{\partial}{\partial r}$ $-\left[\frac{(1+k)}{4}r^2+\frac{t}{2}\right]c^0\frac{\partial}{\partial c^0}$; $X_4=t\frac{\partial}{\partial r}-\frac{(1+k)}{2}rc^0\frac{\partial}{\partial c^0}$; $X_5=\frac{\partial}{\partial r}$; $X_6=c^0\frac{\partial}{\partial c^0}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}+\frac{c^0}{p}\cdot\frac{\partial}{\partial c^0}$; $X_3=r\frac{\partial}{\partial r}-\frac{2c^0}{p}\cdot\frac{\partial}{\partial c^0}$; $X_4=\frac{\partial}{\partial r}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}-\frac{1}{b}\cdot\frac{\partial}{\partial c^0}$; $X_3=r\frac{\partial}{\partial r}-\frac{2}{b}\cdot\frac{\partial}{\partial c^0}$; $X_4=\frac{\partial}{\partial r}$	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}$; $X_3=\frac{\partial}{\partial r}$
$\nu=1$	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}-c^0\frac{\partial}{\partial c^0}$; $X_3=t^2\frac{\partial}{\partial t}+tr\frac{\partial}{\partial r}$ $-\left[\frac{(1+k)}{4}r^2+t\right]c^0\frac{\partial}{\partial c^0}$; $X_4=c^0\frac{\partial}{\partial c^0}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}+\frac{c^0}{p}\cdot\frac{\partial}{\partial c^0}$; $X_3=0$; $X_4=r\frac{\partial}{\partial r}-\frac{2c^0}{p}\cdot\frac{\partial}{\partial c^0}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}+\frac{1}{b}\cdot\frac{\partial}{\partial c^0}$; $X_3=r\ln r\frac{\partial}{\partial r}$ $-\frac{2}{b}(\ln r+1)\frac{\partial}{\partial c^0}$; $X_4=r\frac{\partial}{\partial r}-\frac{2}{b}\cdot\frac{\partial}{\partial c^0}$	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}$
$\nu=2$	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}-\frac{3}{2}c^0\frac{\partial}{\partial c^0}$; $X_3=t^2\frac{\partial}{\partial t}+tr\frac{\partial}{\partial r}-\left[\frac{(1+k)}{4}r^2+\frac{3}{2}t\right]c^0\frac{\partial}{\partial c^0}$;	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}+\frac{c^0}{p}\cdot\frac{\partial}{\partial c^0}$; $X_3=0$; $X_4=r\frac{\partial}{\partial r}-\frac{2c^0}{p}\cdot\frac{\partial}{\partial c^0}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}+\frac{1}{b}\cdot\frac{\partial}{\partial c^0}$;	$X_1=\frac{\partial}{\partial t}$; $X_2=2t\frac{\partial}{\partial t}+r\frac{\partial}{\partial r}$

	$X_4 = t\frac{\partial}{\partial r} - \left(\frac{t}{r} + \frac{(1+k)}{2} r\right) c^0 \frac{\partial}{\partial c^0}$; $X_5 = \frac{\partial}{\partial r} - \frac{c^0}{r} \cdot \frac{\partial}{\partial c^0}$; $X_6 = c^0 \frac{\partial}{\partial c^0}$		$X_3 = 0$; $X_4 = r\frac{\partial}{\partial r}$ $- \frac{2}{b} \cdot \frac{\partial}{\partial c^0}$	
$\nu \neq 0$ $\nu \neq 1$ $\nu \neq 2$	$X_1 = \frac{\partial}{\partial t}$; $X_2 = 2t\frac{\partial}{\partial t} + r\frac{\partial}{\partial r}$ $- \frac{1+\nu}{2} c^0 \frac{\partial}{\partial c^0}$; $X_3 = t^2 \frac{\partial}{\partial t}$ $+ tr\frac{\partial}{\partial r} - \left[\frac{r^2(1+k)}{4} + \frac{1+\nu}{2} t\right] c^0 \frac{\partial}{\partial c^0}$; $X_4 = c^0 \frac{\partial}{\partial c^0}$	$X_1 = \frac{\partial}{\partial t}$; $X_2 = t\frac{\partial}{\partial t} + \frac{c^0}{p} \cdot \frac{\partial}{\partial c^0}$; $X_3 = 0$; $X_4 = r\frac{\partial}{\partial r} - \frac{2c^0}{p} \cdot \frac{\partial}{\partial c^0}$ for $p = \frac{2(2-\nu)}{(\nu-1)}$ $X_1 = \frac{\partial}{\partial t}$; $X_2 = t\frac{\partial}{\partial t} + \frac{c^0}{p} \cdot \frac{\partial}{\partial c^0}$; $X_3 = \frac{r^{(2-\nu)}}{(1-\nu)(2-\nu)} \cdot \frac{\partial}{\partial r}$ $+ \frac{r^{(1-\nu)} c^0}{(2-\nu)} \cdot \frac{\partial}{\partial c^0}$; $X_4 = r\frac{\partial}{\partial r} - \frac{(1-\nu) c^0}{(2-\nu)} \cdot \frac{\partial}{\partial c^0}$	$X_1 = \frac{\partial}{\partial t}$; $X_2 = t\frac{\partial}{\partial t} + \frac{1}{b} \cdot \frac{\partial}{\partial c^0}$; $X_3 = 0$; $X_4 = r\frac{\partial}{\partial r} - \frac{2}{b} \cdot \frac{\partial}{\partial c^0}$	$X_1 = \frac{\partial}{\partial t}$; $X_2 = 2t\frac{\partial}{\partial t} + r\frac{\partial}{\partial r}$
	Single-parameter subgroups for $1<\nu<2$ (k, q_0^0, p, b, α—const)			
	$X_1 + \alpha X_4$; $X_2 + \alpha X_4$; $X_3 + \alpha X_4$; $X_1 - X_2 + \alpha X_4$; $-X_2 + X_3 + \alpha X_4$; $X_1 + X_3 + \alpha X_4$; X_4	$\alpha X_1 + X_4$; $\alpha X_2 + X_4$	$\alpha X_1 + X_4$; $\alpha X_2 + X_4$	X_1; X_2

From conditions (7) we obtain a system of transcendental determining equations:

$$\alpha_0 = \infty, \quad \alpha_{n+1} = 0 \quad (c_0^* = 0, \; c_{n+1}^* = c_0^0),$$
$$\gamma_i \exp(-\alpha_i^2)\left[\frac{c_i^* - c_{i-1}^*}{\operatorname{erf}(\alpha_i) - \operatorname{erf}(\alpha_{i-1}\gamma_{i-1})}\right] = \exp(-\alpha_i^2\gamma_i^2)\left[\frac{c_{i+1}^* - c_i^*}{\operatorname{erf}(\alpha_{i+1}) - \operatorname{erf}(\alpha_i\gamma_i)}\right]. \tag{11}$$

Solution (9) is valid for short time intervals $t \le (1 + k_1)$ and finite grain dimensions or for any lengths of time and large grains ($a \to \infty$), when the symmetry condition (2) at the grain center ($r = 0$) may be disregarded. The symmetry condition can be replaced here by the condition $c_1^0(r, t)|_{r=0} = 0$. For grains of finite dimensions this condition yields an estimate of the time after which solution (9) becomes valid.

For any time and for grains of any dimensions with an arbitrary symmetry parameter ν ($1 < \nu < 2$) we obtain, with the aid of the subgroup $X_2 + \alpha X_4$, the automorphic solution $y_i = \sqrt{\frac{1+k_i}{4t}}\, r$,

$$c_i^0(r, t) = t^{\left(\frac{\alpha}{2} - \frac{1+\nu}{4}\right)}\left[A_i\Phi\left(\frac{1+\nu-2\alpha}{4}, \frac{1+\nu}{2}, -y_i^2\right) + B_i y_i \Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{3-\nu}{2}, -y_i^2\right)\right]. \tag{12}$$

Taking into account conditions (2) and (6), we obtain

$$\begin{aligned}
&\lim_{t\to 0}\left[t^{\left(\frac{\alpha}{2} - \frac{1+\nu}{2}\right)} F_1\right] = 0, \quad A_1 = c_1^* t^{\left(\frac{1+\nu}{4} - \frac{\alpha}{2}\right)} F_1^{-1},\\
&F_i = \Phi\left(\frac{1+\nu-2\alpha}{4}, \frac{1+\nu}{2}, -\alpha_i^2\right),\\
&A_i = t^{\left(\frac{1+\nu}{4} - \frac{\alpha}{2}\right)} \frac{(\alpha_{i-1} c_i^* H_{i-1}^* - \alpha_i c_{i-1}^* H_i)}{(\alpha_{i-1} F_i H_{i-1}^* - \alpha_i H_i F_{i-1}^*)},\\
&F_i^* = \Phi\left(\frac{1+\nu-2\alpha}{4}, \frac{1+\nu}{2}, -\alpha_i^2\gamma_i^2\right),\\
&B_i = t^{\left(\frac{1+\nu}{4} - \frac{\alpha}{2}\right)} \frac{(c_{i-1}^* F_i - c_i^* F_{i-1})}{(\alpha_{i-1} F_i H_{i-1}^* - \alpha_i H_i F_{i-1}^*)},\\
&H_i = \Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{3-\nu}{2}, -\alpha_i^2\right),\\
&H_i^* = \Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{3-\nu}{2}, -\alpha_i^2\gamma_i^2\right).
\end{aligned} \tag{13}$$

From the boundary conditions (7) follows

$$\begin{aligned}
&A_i\left(\frac{1}{2} + \frac{\alpha}{1+\nu}\right)\Phi\left(\frac{1+\nu-2\alpha}{4}, \frac{3+\nu}{2}, -\alpha_i^2\right)\\
&+ B_i\left[\left(\frac{1-\nu}{2}\right)\alpha_i^{-(1+\nu)}\,\Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{3-\nu}{2}, -\alpha_i^2\right)\right.\\
&\left.+\left(\frac{1}{2} + \frac{\alpha}{3-\nu}\right)\Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{5-\nu}{2}, -\alpha_i^2\right)\right]\\
&= A_{i+1}\left(\frac{1}{2} + \frac{\alpha}{1+\nu}\right)\Phi\left(\frac{1+\nu-2\alpha}{4}, \frac{3+\nu}{2}, -\alpha_i^2\gamma_i^2\right)\\
&+ B_{i+1}\left[(\alpha_i\gamma_i)^{-(1+\nu)}\left(\frac{1-\nu}{2}\right)\Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{3-\nu}{2}, -\alpha_i^2\gamma_i^2\right)\right.\\
&\left.+\left(\frac{1}{2} + \frac{\alpha}{3-\nu}\right)\Phi\left(\frac{3-\nu-2\alpha}{4}, \frac{5-\nu}{2}, -\alpha_i^2\gamma_i^2\right)\right].
\end{aligned} \tag{14}$$

From Eqs. (13) and (14) we obtain a transcendental system of equations for determining α_i. By varying the arbitrary parameter α, one can modify the function $c_0(t)$ in the boundary conditions (2).

The sorption dynamics in a porous undeformed medium can be described by the continuity equation and by the equation of diffusive sorption kinetics [15]:

$$\frac{\partial c(z',\ t')}{\partial t'}+\frac{\partial u(z')\,c(z',\ t')}{\partial z'}+\delta\,\frac{\partial q(z',\ t')}{\partial t'}=\frac{\partial}{\partial z'}\left[D'(u)\,\frac{\partial c(z',\ t')}{\partial z'}\right], \tag{15}$$

$$\frac{\partial q(z',\ t')}{\partial t'}=\beta(u)\,[c(z',\ t')-f(q(z',\ t'))], \tag{16}$$

where, according to [16-19],

$$\frac{1}{\beta(u)}=\frac{a^2}{(\nu+1)(\nu+3)D_i}+\frac{a}{(\nu+1)\beta_0(u)},$$
$$D'(u)=D_g+D_1u+D_2u^2,$$

with the zero initial and boundary conditions

$$c(z',\ t')|_{z'=0}=c_0^0=\mathrm{const}\ (\text{frontal sorption dynamics}) \tag{17}$$

$$c(z',\ t')|_{z'=0}=c_0^0\delta(t)\ (\text{elutive sorption dynamics})$$
$$\text{at}\quad c(z',\ t')|_{z'=0}=c_0^0[1-\eta(t'-t_0')]. \tag{18}$$

In order to set up continuous Lie groups, we will seek the following infinitesimal operator:

$$X=\xi\,\frac{\partial}{\partial t}+\eta\,\frac{\partial}{\partial z}+\sigma\,\frac{\partial}{\partial q}+\tau\,\frac{\partial}{\partial c}.$$

When $u(z')\neq\mathrm{const}$, system (15)-(16) will be rewritten in dimensionless variables:

$$\frac{\partial c}{\partial t}+\varphi_1\frac{\partial c}{\partial z}+\varphi_2c+\delta\,\frac{\partial q}{\partial t}=\varphi_3\frac{\partial^2c}{\partial z^2},\quad \frac{\partial q}{\partial t}=c-f(q), \tag{19}$$

where

$$t=\beta(u)\,t',\quad z=\int\limits_0^z\frac{\beta(u)}{u}\,dz',\quad D=D'(u)\,\beta(u)\,u^{-1},$$

$$\varphi_2=\frac{1}{u}\cdot\frac{du}{dz},\quad \varphi_3=\frac{D}{u},\quad \varphi_1=1-\frac{1}{u}\cdot\frac{dD}{dz}=1-\varphi_3\varphi_2.$$

System (19) for an arbitrary isotherm $q = f(c)$ allows a unique operator $\partial/\partial t + w(\partial/\partial z)$ (operator of Galilean transfer with the front of the sorption wave traveling at the velocity w) at φ_1, φ_2, φ_3 = const. For such an operator the invariant solution $y = z - wt$ allows us to reduce (19) to the system

$$-w\,\frac{dc}{dy}+\varphi_1\frac{dc}{dy}+\varphi_2c-\delta w\,\frac{dq}{dy}=\varphi_3\frac{d^2c}{dy^2},\quad -w\,\frac{dq}{dy}=c-f(q), \tag{20}$$

$$c(-\infty)=c_0^0=f(q_0^0),\quad q(-\infty)=q_0^0,\quad c(+\infty)=q(+\infty)=0,$$
$$\left(\frac{dc}{dy}=\frac{dq}{dy}\right)\bigg|_{y\to\pm\infty}=0. \tag{21}$$

System (20) is compatible only when $\varphi_1 = 0$. Consequently, no parallel transfer mode exists when $u(z') \neq \mathrm{const}$.

When $u(z') = \mathrm{const}$, system (15)-(16) in dimensionless variables becomes

$$\frac{\partial c}{\partial t}+\frac{\partial c}{\partial z}+\delta\,\frac{\partial q}{\partial t}=D\,\frac{\partial^2c}{\partial z^2},\quad \frac{\partial q}{\partial t}=c-f(q),$$
$$t=\beta(u)\,t',\quad z=\frac{\beta(u)\,z'}{u},\quad D=\frac{D'(u)\,\beta(u)}{u^2}. \tag{22}$$

TABLE 2. Infinitesimal Operators and Single-Parameter Subgroups Allowable in Terms of Eq. (26) (q_0^*, q_0, q_0^0, f_0, $\varkappa$, b = const)

Arbitrary f	$X_1=\frac{\partial}{\partial t}$; $X_2=0$; $X_3=\frac{\partial}{\partial z}$	X_1+wX_3
$f=\frac{f_0}{\varkappa}\exp(\varkappa q)$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}-\frac{1}{\varkappa}\cdot\frac{\partial}{\partial q}$; $X_3=\frac{\partial}{\partial z}$	X_1+wX_3; $X_2+\alpha X_3$
$f=\frac{f_0}{(1+b)}q^{(1+b)}$	$X_1=\frac{\partial}{\partial t}$; $X_2=t\frac{\partial}{\partial t}-\frac{q}{b}\cdot\frac{\partial}{\partial q}$; $X_3=\frac{\partial}{\partial z}$	X_1+wX_3; $X_2+\alpha X_3$
$f=\frac{q}{k}$	$X_1=-z\frac{\partial}{\partial z}+t\frac{\partial}{\partial t}+\left(\delta z-\frac{t}{k}\right)q\frac{\partial}{\partial q}$;	X_1; $X_2+\alpha X_3$
	$X_2=\frac{\partial}{\partial z}$; $X_3=\frac{\partial}{\partial t}$; $X_4=q\frac{\partial}{\partial q}$	X_1+X_2; X_1+X_3; X_4

For an arbitrary isotherm the system (22) allows a unique operator $\partial/\partial t + w(\partial/\partial z)$. The invariant solution $y = z - wt$ allows us to reduce the system (22) of partial differential equations to a system of ordinary differential equations. After integrating, with conditions (21) taken into account, we obtain

$$(1-w)c+\delta wq=D\frac{dc}{dy},\quad -w\frac{dq}{dy}=c-f(q),\quad w=\frac{c_0^0}{c_0^0+\delta q_0^0}. \tag{23}$$

It has been shown in [13] that, when D = 0, system (22) with the boundary conditions (17) has an asymptotic solution, for a convex isotherm, which is a sorption wave traveling at the velocity w. It can also be shown that, when $D \neq 0$, system (22) with the boundary conditions (17) admits a physically feasible solution for a convex isotherm, which is a sorption wave.

In some applications [13, 20, 21] one often uses the approximate system (15)-(16) at $D \sim 0$. Asymptotic approximations of the equations of sorption dynamics can be set up in another way. Indeed, since in the case of elutive sorption dynamics (18) one considers the propagation of a $\delta(t)$ perturbation in a porous medium ("dispersing" $\delta(t)$ perturbations will follow a quasi-Gaussian distribution curve whose shape is determined by a given first initial and three central moments), it seems reasonable to use in the case of a linear isotherm the expressions for the moments as the accuracy criteria for the equations in [16]. The equations which have been obtained for a linear isotherm can be generalized for a nonlinear one [16]. It can be shown that, in the first asymptotic approximation, system (15)-(16) is – with respect to accuracy – equivalent to the system

$$\frac{\partial c}{\partial z}+\delta\frac{\partial q}{\partial t}=0,\quad \frac{\partial q}{\partial t}=c-f(q), \tag{24}$$

where

$$t=\beta^*t'-\frac{\beta^*z'}{u},\quad z=\frac{z'\beta^*}{u},\quad \frac{1}{\beta^*}=\frac{1}{\beta(u)}+\frac{\delta D'(u)}{u^2},$$

or to the equation

$$\frac{\partial c}{\partial t}+\frac{\partial c}{\partial z}+\delta\frac{\partial q}{\partial t}=\frac{\partial^2 c}{\partial z^2},\quad q=f(c), \tag{25}$$

where

$$t=\frac{t'u^2}{D^*},\quad z=\frac{z'u}{D^*},\quad D^*=D'(u)+\frac{u^2}{\delta\beta(u)}.$$

System (24) yields the equation

$$\frac{\partial^2 q}{\partial z\partial t}+\frac{df}{dq}\cdot\frac{\partial q}{\partial z}+\delta\frac{\partial q}{\partial t}=0. \tag{26}$$

In Table 2 are given the infinitesimal operators and single-parameter subgroups of these operators, allowable in terms of Eq. (26). For a nonlinear isotherm, the operator of Galilean transfer $X_1 + wX_3$ has an invariant solution, since this operator yields from (24) a compatible system of equations. The invariant solutions for a linear isotherm will not be analyzed here, because the constraint problem can in this case be solved by the Riemann method or by means of the Laplace transformation. For a nonlinear isotherm

$f = (f_0/\varkappa)\exp(\varkappa q)$, the subgroup $X_2 + \alpha X_3$ yields the invariant solution $y = t\exp(-z/\alpha)$, $q = -z/\varkappa\alpha + L(y)$,

$$c = \exp\left(-\frac{z}{\alpha}\right)\left[\frac{dL}{dy} + \frac{f_0}{\varkappa}\exp(\varkappa L)\right], \quad c\,|_{z=0} = \frac{dL}{dt} + \frac{f_0}{\varkappa}\exp(\varkappa L). \tag{27}$$

From (26) we find the ordinary differential equation for determining the function $L(y)$:

$$y\frac{d^2L}{dy^2} + \frac{dL}{dy}[1 - \delta\alpha + yf_0\exp(\varkappa L)] + \frac{f_0}{\varkappa}\exp(\varkappa L) = 0, \tag{28}$$

$$\lim_{t\to 0}\left[\frac{dL}{dt} + \frac{f_0}{\varkappa}\exp(\varkappa L)\right] = 0. \tag{29}$$

Condition (29) corresponds to the zero initial conditions. Equations (25) and (26) are valid for asymptotically large time intervals and column lengths and, consequently, the invariant solutions to (28) and the analogous solutions which will be considered subsequently are the solutions to the constraint problems with conditions (27). One may consider in the first approximation, however, that the asymptotic solutions are weakly dependent on the form of the boundary conditions and the "ideal" step conditions (17)-(18) will be transformed so as to put the asymptotic solutions in the form (27). The choice of the arbitrary parameter α makes various solutions feasible.

A nonlinear isotherm $f = (f_0/(1+b))q^{(1+b)}$ has the subgroup $X_2 + \alpha X_3$ which yields the invariant solutions $y = t\exp(-z/\alpha)$,

$$q = \exp\left(-\frac{z}{\alpha}\right)L(y), \quad c = \exp\left[-\frac{z(1+b)}{\alpha b}\right]\left(\frac{dL}{dy} + \frac{f_0}{1+b}L^{(1+b)}\right),$$

$$c\,|_{z=0} = \frac{dL}{dt} + \frac{f_0}{1+b}L^{(1+b)}$$

and a corresponding equation for $L(y)$ with the condition

$$\begin{gathered} y\frac{d^2L}{dy^2} + \left[1 + \frac{1}{b} - \delta\alpha + f_0 yL^b\right]\frac{dL}{dy} + \frac{\alpha}{b}f_0 L^{(1+b)} = 0, \\ \lim_{t\to 0}\left[\frac{dL}{dt} + \frac{f_0}{1+b}L^{(1+b)}\right] = 0. \end{gathered} \tag{30}$$

In Table 3 are given the infinitesimal operators and single-parameter subgroups of these operators, allowable in terms of Eq. (25). For an arbitrary isotherm, Eq. (25) admits the operator $X_1 + wX_3$, which corresponds to a parallel transmission of a sorption wave at the velocity w. For the invariant solution $y = z - wt$ at a convex isotherm, Eq. (25) yields after integration:

$$\begin{gathered} y = \varphi(c) - y_0 = \varphi(c) - \frac{1}{c}\int_0^c \varphi(x)\,dx, \quad \varphi(c) = \int\frac{dc}{(1-w)c + \delta wq(c)}, \\ w = \frac{c_0^0}{c_0^0 + \delta q_0^0}. \end{gathered} \tag{31}$$

The integration constant y_0 is found from the integral version of Eq. (25).

For an isotherm $q = q_0^* - c/\delta + (q_0^0/\varkappa\delta)\exp(\varkappa c)$, the subgroup $X_2 + \alpha X_3$ yields the invariant solution $y = t\exp(-z/\alpha)$, $c = (1/\varkappa)\ln y + L(y)$, $c|_{z=0} = (1/\varkappa)\ln t + L(t)$, and, accordingly, the equation and condition for $L(y)$:

$$\begin{gathered} y^2\frac{d^2L}{dy^2} + \frac{dL}{dy}[y(1-\alpha) + q_0^0\alpha^2\exp(\varkappa L)] + \frac{\alpha^2}{\varkappa}q_0^0\exp(\varkappa L) = 0, \\ \lim_{t\to 0}\left[\frac{1}{\varkappa}\ln t + L(t)\right] = 0. \end{gathered} \tag{32}$$

TABLE 3. Infinitesimal Operators and Single-Parameter Subgroups Allowable in Terms of Eq. (25)

Arbitrary q	$X_1 = \frac{\partial}{\partial t};\ X_2 = 0;\ X_3 = \frac{\partial}{\partial z}$	$X_1 + wX_3$
$q = q_0^* - \frac{c}{\delta} + \frac{q_0^0}{\delta\varkappa}\exp(\varkappa c)$	$X_1 = \frac{\partial}{\partial t};\ X_2 = t\frac{\partial}{\partial t} + \frac{1}{\varkappa}\cdot\frac{\partial}{\partial c};\ X_3 = \frac{\partial}{\partial z}$	$X_1 + wX_3$; $X_2 + \alpha X_3$
$q = q_0^* - \frac{c}{\delta} + \frac{q_0}{\delta(1+b)}c^{(1+b)}$	$X_1 = \frac{\partial}{\partial t};\ X_2 = t\frac{\partial}{\partial t} + \frac{c}{b}\cdot\frac{\partial}{\partial c};\ X_3 = \frac{\partial}{\partial z}$	$X_1 + wX_3$; $X_2 + \alpha X_3$
$q = kc$	$X_1 = \frac{\partial}{\partial t} - \frac{c}{4(1+\delta k)}\cdot\frac{\partial}{\partial c};\ X_2 = t\frac{\partial}{\partial t} + \frac{z}{2}\frac{\partial}{\partial z} + c\left(\frac{z}{4} - \frac{1}{4} + \frac{t}{4(1+\delta k)}\right)\frac{\partial}{\partial c};$ $X_3 = t^2\frac{\partial}{\partial t} + zt\frac{\partial}{\partial z} + c\left[\frac{zt}{2} - \frac{t}{2} - \frac{t^2}{4(1+\delta k)} - \frac{(1+\delta k)}{4}z^2\right]\frac{\partial}{\partial c};$ $X_4 = t\frac{\partial}{\partial z} + c\left(\frac{t}{2} - \frac{1+\delta k}{2}z\right)\frac{\partial}{\partial c};$ $X_5 = \frac{\partial}{\partial z} + \frac{c}{2}\cdot\frac{\partial}{\partial c};\ X_6 = c\frac{\partial}{\partial c}$	X_1; X_2; $X_3 + X_4 + X_5$; X_3; X_4; $X_4 + X_5$; X_5; $X_1 + X_4 + X_5 + X_6$; $X_1 + X_3$; $X_3 + X_6$; $X_1 + X_2$; X_6

For an isotherm $q = q_0^* - c/\delta + (q_0^0/\delta(1+b))c^{(1+b)}$, the subgroup $X_2 + \alpha X_3$ yields the invariant solution $y = t\exp(-z\ \ \alpha)$, $c = \exp(z/b\alpha)L(y)$, $c|_{z=0} = L(t)$, and the equation and condition for $L(y)$:

$$y^2\frac{d^2L}{dy^2} - \frac{dL}{dy}\left[q_0^0\alpha^2L^b + y\left(\frac{2}{b} - 1 - \alpha\right)\right] + L\left(\frac{1}{b^2} - \frac{\alpha}{b}\right) = 0, \qquad (33)$$
$$L(0) = 0.$$

Equations (28), (30), (32), and (33) are integrable without difficulty or solvable in various approximations.

NOTATION

$c^0(r, t)$	is the concentration of a substance (sorbate) inside a porous grain of a sorbent;
$q^0(r, t)$	is the concentration of a substance adsorbed by the inner surface of a porous grain;
$t = t'D_i/a^2$;	
$r = r'/a$;	
t', r'	are the dimensional independent variables;
$\varkappa = D_i/a\beta_0$;	
c	is the concentration of sorbate in the stream;
u	is the superficial flow velocity;
$\delta = \delta_0/(\nu - 1)$;	
$\delta_0 = (1-\sigma)/\sigma$;	
σ	is the fraction of the free column space filled with granular sorbent grains;
β_0	is the coefficient of (external) mass transfer at the outer surface of a sorbent grain;
q	is the mean-over-the-grain concentration of the absorbed substance;
D'	is the dispersion factor accounting for the longitudinal stirring effect;
D_i	is the diffusivity inside narrow channels of a sorbent grain;
k_1, k_2	are the sorption and desorption coefficient, respectively;
$k = k_1/k_2$;	
ν	is the symmetry parameter ($\nu = 2$ for a sphere with a radius a; $\nu = 1$ for a cylinder with a radius a, $\nu = 0$ for a plate with a thickness $2a$);
$\delta(t)$	is the delta function;
$\eta(t)$	is the unit-step function.

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