TRANSPORT RELAXATION AND STEADY-STATE STABILITY IN AN ISOTHERMAL FLOW REACTOR

A. I. Moshinskii

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Stagnant volumes, cavities between grains, etc., influence the steady-state stability in an isothermal flow reactor. Mass transfer between the stagnant and flow regions may be described via relaxation equations in fairly general form. Equations and algorithms are given for defining the steady-state stability, and examples are considered.

Introduction. Production organization requires the determination of stationary states and stability in chemical reactors. In numerous theoretical studies, this has been examined mainly for two limiting states, ideal displacement and ideal mixing. In addition, it is traditional to neglect the separate circulation zones that may exist in a reactor and the relaxation in mass transfer in granular catalyst beds.

Here is shown that these features can be incorporated in stability determination in a simple fashion. Considerable importance attaches to the additional conditions, and as there are some disagreements on this in the literature, we examine the topic for the boundary condition at the reactor inlet.

1. Reactor Inlet Boundary Condition. Here is briefly discussed the usual boundary condition for the inlet to a reactor or granular bed:

$$D\partial C/\partial X|_{X=0}=U(C-C_0), \tag{1}$$

in which C_0 is the concentration in the inlet flow, U the transport rate, and D the effective diffusion (dispersion) coefficient. As the last decreases to the molecular diffusion coefficient D_* for $X \to 0$ [1, 2], condition (1) should contain D_* instead of D, which with the usual situation $D_* \ll D$ leads to $C|_{X=0} = C_0$, which is proposed as the boundary condition. On the other hand, D is used in the basic dispersion equation. Then one has a natural choice of an equation with constant D (the range in which D is dependent on X for $X \to 0$ is not considered), but there is an ambiguity in choosing the boundary condition for $X \to 0$.

In the usual case where the zone for transition from D_* to D is short, condition (1) is best. For definiteness, we take the equation for the diffusion model in the traditional form

$$D\frac{\partial}{\partial X}\left[E(X)\frac{\partial C}{\partial X}\right]-U\frac{\partial C}{\partial X}=\frac{\partial C}{\partial \tau}+\Phi(C);\ X\in(0,\ l), \tag{2}$$

in which $\Phi(C)$ characterizes the reaction rate as a function of concentration, with l the reactor length; E is a fairly general function subject to the condition for sharp change in the section $[0, \Delta]$, where $\Delta \ll l$, and for $X \geq \Delta$: $E(X) \approx 1$, $E'(X) \ll 1$, and at $X = 0$: $E(0) = D_*/D$. The inlet boundary condition is

$$D_*\partial C/\partial X|_{X=0}=U(C-C_0) \tag{3}$$

and is then not subject to doubt. The other conditions for uniqueness are not required for (2).

The two small parameters $\Delta/l \ll 1$ and $D_*/D \ll 1$ enable one to use perturbation theory [3] in order to establish the inlet boundary condition for

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$$D\partial^2C/\partial X^2 - U\partial C/\partial X = \partial C/\partial\tau + \Phi(C), \tag{4}$$

which can be considered as external [3] in the region $\Delta \ll X \leq \ell$. Here D = const. However, a simpler approach is as follows. We integrate (2) with respect to X with limits [0, Δ]:

$$D\left.\frac{\partial C}{\partial X}\right|_{X=\Delta} - UC|_{X=\Delta} = D_*\left.\frac{\partial C}{\partial X}\right|_{X=0} - UC|_{X=0} + \int_0^\Delta \left[\frac{\partial C}{\partial \tau} + \Phi(C)\right] dX. \tag{5}$$

In the ordinary situation, the term in the integral in (5) is the order of one, so the entire integral is of the order of Δ, and as $\Delta \ll \ell$, (1) follows closely from (5) and (3), where it is desirable to replace Δ by zero in the final form of the boundary condition, i.e., to displace the origin somewhat. The physical significance of that conclusion relates to material balance for a layer of thickness Δ, within which the dispersion coefficient is dependent on X. The concentration changes within the layer are negligible by comparison with the fluxes at the layer boundaries.

2. Formulation and Analysis. We now consider the steady-state stability. The basic equation is taken as

$$\frac{1}{\mathrm{Pe}}\frac{\partial^2 c}{\partial X^2} - \frac{\partial c}{\partial X} - \alpha\varphi(c) = \alpha\frac{\partial c}{\partial t} + (1-\alpha)\frac{\partial}{\partial t}\int_0^t K(t-\xi)\,c(x,\ \xi)\,d\xi, \tag{6}$$

in which α is the flow part of the reactor as a function of the total volume, $c = C/C_0$, $\mathrm{Pe} = U\ell/D$ is the Peclet number, and $\varphi(c) = \ell\Phi(C)/UC_0$; $x = X/\ell$. K(t) describes the relaxation in mass transfer between the flow section and the stagnant volumes. We assume that K is independent of x, and the common case in practice is where the mass transfer between the flow section and the stagnant zones is described by the following kinetic equation [4]:

$$(1-\alpha)\,\mathrm{Pe}\,\partial c_1/\partial l = \varkappa(c - c_1),\ \varkappa = \mathrm{const} > 0, \tag{7}$$

or a simple extension to the case of unequal exchange rates in the forward and reverse directions. The integral in (6) coincides with c_1, the concentration in the stagnant zones. Eliminating c_1 from (7) gives the kernel K as an exponential: $K(t) = [\varkappa/\mathrm{Pe}(1-\alpha)]\exp[-\varkappa t/\mathrm{Pe}(1-\alpha)]$, but the formulas for K in some other cases can be more complicated [5-7].

We now assume that K(t) is such that the relaxation term in (6) becomes zero for $t \to \infty$ along with $\alpha\partial c/\partial t$, so the system goes over to one of the stationary states implied from the initial conditions for (6). The boundary conditions for (6) are standard:

$$\mathrm{Pe}^{-1}\partial c/\partial x|_{x=0} = c - 1,\ \partial c/\partial x|_{x=1} = 0, \tag{8}$$

where the second condition is the Dankwerth one and the first is the dimensionless form of (1), so the stationary solution $c = c_*(x)$ satisfies

$$\mathrm{Pe}^{-1}d^2c_*/dx^2 - dc_*/dx = \alpha\varphi(c_*),\ x \in (0,\ 1), \tag{9}$$

and (8). Solutions for particular φ(c) have been discussed [8-10], where the number of stationary states has also been determined. We subsequently take $c_*(x)$ as a known function.

We linearized (6) near $c_*(x)$ to establish the stability:

$$c = c_*(x) + g(x,\ t)\exp(x\,\mathrm{Pe}/2),\ |g| \ll |c_*(x)|. \tag{10}$$

We substitute (10) into (6) in the linear approximation:

$$\frac{1}{\mathrm{Pe}}\frac{\partial^2 g}{\partial x^2} - \left\{\frac{\mathrm{Pe}}{4} + \alpha\varphi'[c_*(x)]\right\} g = \alpha\frac{\partial g}{\partial t} + (1-\alpha)\frac{\partial}{\partial t}\int_0^t K(t-\xi)\,g(x,\ \xi)\,d\xi. \tag{11}$$

The corresponding boundary conditions for (11) are

$$\partial g/\partial x|_{x=0} = \mathrm{Pe}\,g/2|_{x=0},\ \partial g/\partial x|_{x=1} = -\mathrm{Pe}\,g/2|_{x=1}. \tag{12}$$

The solution to (11) and (12) is the series

$$g(x,\ t) = \sum_{n=1}^{\infty} A_n Z_n(x)\,\Theta_n(t), \tag{13}$$

in which A_n are coefficients defined by the initial condition, and as the initial condition is not required in order to establish the stability, the A_n are not subsequently required. Z_n are eigenfunctions for the Sturm–Liouville treatment for

$$\mathrm{Pe}^{-1}d^2Z_n/dx^2+\{\lambda_n-\mathrm{Pe}/4-\alpha\varphi'[c_*(x)]\}Z_n=0 \tag{14}$$

with the (12) boundary conditions, in which one substitutes for Z_n, while λ_n are the eigenvalues corresponding to Z_n (n = 1, 2, 3, ...). It follows from (11)-(14) that the functions Θ_n satisfy

$$\alpha\frac{d\Theta_n}{dt}+(1-\alpha)\frac{d}{dt}\int_0^t K(t-\xi)\,\Theta_n(\xi)\,d\xi=-\lambda_n\Theta_n. \tag{15}$$

The initial condition for (15) is unimportant ($\Theta_n(0)\neq 0$), as it has no major significance, and a lower limit of 0 in the integrals in (6), (11), and (15) may be replaced by $-\infty$, while the upper one is simultaneously replaced by $+\infty$.

The Sturm–Liouville problem for $Z_n(x)$ coinides with that considered in [10] ($\alpha = 1$), where several examples were examined for particular $\varphi(c)$, and the first (least) eigenvalues λ_1 were determined for them, which in the [10] case [corresponds to (4)], that value was basic to the stability in the stationary state. Then $\lambda_1 < 0$ does not necessarily guarantee instability. One can judge the behavior of the concentration perturbation g from the asymptotic behavior of Θ_1 for $t\to\infty$, since the condition $\lambda_n > \lambda_1$, n = 2, 3, ... [11] implies that for any ordinary function $K(t)\geq 0$, the asyptotes to Θ_n are more favorable for stability. For example, for bounded K(t): $0\leq K_-\leq K(t)\leq K_+$, from (15) one readily gets

$$\exp\{-t[\lambda_n+(1-\alpha)K_+]/\alpha\}\leqslant\Theta_n(t)/\Theta_n(0)\leqslant$$
$$\leqslant\exp\{-t[\lambda_n+(1-\alpha)K_-]/\alpha\}, \tag{16}$$

which also implies that relaxation effects stabilize the system. We do not consider other possible constraints on K(t) and give preference to the K(t) usually found in practice, where the functions are subject to natural (physical) requirements.

We further assume that K(t) has the Laplace transform K*(p), in which the asterisk relates to the transformed quantities and p is the variable. We apply it to (15) and assume for simplicity that $\Theta_n(0) = 1$ to get

$$\Theta^*(p)=\alpha\{p[\alpha+(1-\alpha)K^*(p)]+\lambda\}^{-1}, \tag{17}$$

in which the subscript n has been omitted. Inverting (17) is dependent on the structure of K*(p). If it is a single-valued function, the behavior of $\Theta(t)$ for $t\to\infty$ is governed by the residue of $\Theta^*(p)\exp(pt)$ at the singular point having the largest real part: $p = p_*$, in which p_* is the root of

$$p_*[\alpha+(1-\alpha)K^*(p_*)]+\lambda=0, \tag{18}$$

where one assumes that the integration path in the Riemann–Mellin formula can be transformed in such a way as to provide appropriate behavior for the integrand function for $p\to\infty$ in a certain sector of the complex variable p [12]. If K*(p) has branch points, one should consider definite integrals related to the corresponding sections between such points. Such integrals usually tend to zero for $t\to\infty$. Equation (18) in any form is of basic significance to the stability.

If K*(p) is a fractionally rational function, the stability analysis can be based on familiar methods and tests [13] widely used in automatic control. The parameter fluctuations (noise) usual in such systems are assumed to be slight and not capable of affecting the qualitative behavior, as has recently been pointed out [14, 15].

3. Limiting Forms. To consider limiting cases, we assume that all the parameters apart from the limiting one are of the order of one, in order to avoid possible nonuniformities in the expansions, although sometimes it is simpler to consider the parameter angle where uniformity is not disrupted.

One usually tends not to assume that there are stagnant zones, so interest attaches to the case of α close to one, when the root of (18) can be found approximately by perturbation methods [3] by reference to $1-\alpha$:

$$p_* = -\lambda + (1-\alpha)\lambda[K^*(-\lambda) - 1] + O[(1-\alpha)^2],\ \alpha \to 1-0. \tag{19}$$

Stability occurs for $\mathrm{Re}\, p_* < 0$. A shift in p_* relative to the form without relaxation $K^* = 0$ constitutes $(1-\alpha)\lambda K^*(-\lambda)$, i.e., in the absence of stability ($\lambda < 0$) and what occurs for $K(t) \geq 0$ with the inequality $K^*(p) > 0$ for real $p > 0$, so relaxation stabilizes the reactor. Stagnant zones ($\alpha \neq 1$) stabilize the system but reduce the active zone for the reaction by a factor α [the α factor with $\varphi(c)$ in (6)].

The second limiting form is ideal displacement, $\mathrm{Pe} \to \infty$:

$$c_* = G(x) + \mathrm{Pe}^{-1}\alpha\varphi[G(1)] \exp[\mathrm{Pe}\,(x-1)], \tag{20}$$

has G(x) the inversion of the integral

$$\alpha x = \int_G^1 d\xi/\varphi(\xi), \tag{21}$$

and on substitution into (9) and (8) satisfies them with an error of the order of Pe^{-1}, which tends to zero. If the (21) integral converges within (0, 1) limits, one assumes that its value exceeds α, which is a guarantee that G does not become zero in the range (0, 1). As one usually considers φ as sign-constant, (21) will be a monotone function of G, so there is a unique inverse function G(x), i.e., there is a unique stationary state under these conditions.

One cannot use (14) to analyze the stability here because the condition for the perturbation $g \exp(x\,\mathrm{Pe}/2)$ to be small is violated for $\mathrm{Pe} \to \infty$, which makes the subsequent expressions unsound. Here we can examine (6) directly for stability for $\mathrm{Pe} \to \infty$. In the main region in the reactor (far from the boundary layer zone at x = 1), (6) does not contain the diffusion term $\mathrm{Pe}^{-1}\partial^2 c/\partial x^2$, and the linear analog of (11) derived with the $c = G(x) + g(x, t)$, $|g| \ll G$ linearization from (6) is readily analyzed by operational methods. With the initial perturbation $g(x, 0) = g_0(x)$, the expression for g following Laplace transformation with respect to t is

$$g^*(x, p) = \alpha\varphi[G(x)] \int_0^x g_0(\xi)\{\varphi[G(\xi)]\}^{-1} \exp\{p(\xi - x)[\alpha + (1-\alpha)K^*(p)]\}\, d\xi. \tag{22}$$

Inversion of (22) is dependent on the features of $pK^*(p)$ for finite p and for $p \to \infty$, and there are no particular problems in the asymptotic examination of g(x, t) for $t \to \infty$ for the K(t) used in practice. Here $\varphi(c)$ has not effect on the inversion of (22) in the p plane, i.e., the qualitative features are governed only by K(t).

The opposite case $\mathrm{Pe} \to 0$ is more interesting. One uses (6) and constructs the limiting equation as in [16, 17], which gives [c = c(t)]:

$$\frac{d}{dt}\left[\alpha c + (1-\alpha)\int_0^t K(t-\xi)c(\xi)\,d\xi\right] = 1 - c - \alpha\varphi(c). \tag{23}$$

The stationary states $c = c_* = \mathrm{const}(x)$ are defined by

$$\alpha\varphi(c) = 1 - c, \tag{24}$$

and the behavior of the perturbation g, $c = c_* + g(t)$, $|g| \ll c_*$, is described by

$$\frac{d}{dt}\left[\alpha g + (1-\alpha)\int_0^t K(t-\xi)g(\xi)\,d\xi\right] = -g[1 + \alpha\varphi'(c_*)]. \tag{25}$$

Laplace transformation and subsequent steps result in the replacement of (18) by

$$p_*[\alpha + (1-\alpha)K^*(p_*)] + 1 + \alpha\varphi'(c_*) = 0, \tag{26}$$

for determining the stability bounds in relation to the parameters, i.e., here for λ in (18) one obtains an analytic formula dependent on φ and c_*.

This example is readily extended to property inhomogeneity along the reactor, where D, K, and φ are explicitly dependent on x, i.e., $D = D(x, c)$, $K = K(x, t)$, $\varphi = \varphi(x, c)$. The

Peclet number constituted by the minimum possible D should be small, and then (23) is replaced [16, 17] by

$$\frac{d}{dt}\left[\alpha c + (1-\alpha)\int_0^t c(\xi)\,d\xi \int_0^1 K(x,\ t-\xi)\,dx\right] = 1 - c - \alpha\int_0^1 \varphi[x,\ c(t)]\,dx. \tag{27}$$

It will also be simple to incorporate the x dependence of α. The equation for stationary states corresponds to the rhs in (27) being zero for $c(t) = c_*$, and one can also readily extend (25) for the evolution of g, but we do not give the equation.

4. Examples. We first consider mass transfer between the flow section and the stagnant zones as defined by (7), where $K^*(p) = \varkappa/[1-\alpha)p\,\mathrm{Pe} + \varkappa]$, and (18) readily gives the root p_* having the largest real part:

$$p_* = \frac{\sqrt{[\varkappa + \lambda\,\mathrm{Pe}(1-\alpha)]^2 - 4\,\mathrm{Pe}\,\lambda\varkappa\alpha(1-\alpha)} - \varkappa - \lambda\,\mathrm{Pe}(1-\alpha)}{2\,\mathrm{Pe}\,\alpha(1-\alpha)}, \tag{28}$$

where for this branch in the root we have taken $\sqrt{1} = 1$. For $\lambda < 0$, the stagnant volumes tend to stabilize the system.

In the second example, we take K(t) as $K(t) = \beta/\sqrt{\pi t}$, $\beta = \mathrm{const} > 0$, which is a common case [6, 7, 18], and where $K^*(p) = \beta/\sqrt{p}$. Equation (18) gives the root with the largest real part for $\lambda < 0$ as

$$p_* = -\frac{\lambda}{\alpha} + \frac{(1-\alpha)^2\beta^2}{2\alpha^2\lambda} - \frac{(1-\alpha)\beta\sqrt{(1-\alpha)^2\beta^2 - 4\alpha\lambda}}{2\alpha^2\lambda} \tag{29}$$

with the same branch for the square root as in the first example.

If the concentration changes slowly, mass transfer in a two-phase system can be examined from the equivalent equation [6, 7, 19] of elliptic type, for which one can also readily determine the stability limit $\mathrm{Re}\,p_* = 0$. However, the $K^*(p)$ for it is derived as an approximate relation for $p \to 0$ from the $K^*(p)$ in the first example, so we do not consider this case.

Conclusions. We have considered how mass-transfer relaxation between the flow part and the stagnant volumes affects the stability in an isothermal flow reactor. Stability testing requires firstly that one should determine the stationary solution to (9) and then derive the first eigenvalue λ_1 in the Sturm–Liouville problem of (12) and (14). Those topics have been considered in detail in [10]. Then one should determine the root p_* of (18) for the $\lambda = \lambda_1$ with the largest real part. The condition $\mathrm{Re}\,p_* = 0$ represents the stability limit, which is observed for $\mathrm{Re}\,p_* < 0$. With the positive relaxation kernels K(t) usually found in practice, that effect tends to stabilize the stationary states. Studies have also been made on simplifying the procedure for the limiting cases $\alpha \to 1$, $\mathrm{Pe} \to \infty$, $\mathrm{Pe} \to 0$, which are particularly significant in the latter two cases, since those simplifications enable one to avoid employing a numerical procedure [10]. The results can be used in designing isothermal reactors.

NOTATION

C, C_0, reagent concentration and initial value of it; g, concentration perturbation; $t = \tau U/\ell$; X, coordinate along reactor; τ, time; *, Laplace-transformed quantities.

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SENSITIVITY AND SPEED OF RESPONSE OF A SUPERCONDUCTING OPTOELECTRONIC THERMAL RADIATION DETECTOR

O. S. Esikov, A. I. Krot, E. A. Protasov, V. P. Sobolev, and V. S. Kharitonov

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Numerical estimates of the temperature sensitivity and speed of response are obtained for one type of sensing element of a superconducting optoelectronic thermal radiation detector. Possible ways to improve the performance characteristics of such an element are analyzed.

Esikov and Protasov [1] have proposed a new principle for the detection of thermal radiation, described a circuit for its implementation, and estimated the possible sensitivity of an integrated superconducting optoelectronic detector (ISOD) operating on this principle. The subsequent improvement of such systems, particularly in the design of widescreen detectors for moving images, calls for the solution of several problems pertaining to the optimization of their geometrical and thermophysical characteristics with a view toward maximizing the sensitivity, speed of response, and uniformity of the distribution of these parameters over the sensing area. The overall sensitivity of the ISOD is characterized by the product of the permeability variation of the superconducting sensing element per unit heat flux incident on it and the sensitivity of a magnetooptical transducer to a corresponding variation of the heat flux through the sensing element. The possible sensitivity of a magnetooptical transducer has been estimated previously [1]. The ultimate sensitivity of the sensing element depends on the width of the superconducting transition of the superconducting film, the strength of the magnetic field applied to the sensing element, and the thermal resistance of the elements used to create thermal coupling of the superconducting film with the thermostat [2]. The speed of the ISOD is limited mainly by the rise time of the temperature field in the sensing element and by the speed of the counting device.

In the present article we analyze the speed and sensitivity characteristics of the sensing element of a particular ISOD configuration (Fig. 1) with a uniformly illuminated sensing surface. The sensing element is a smooth thin wafer of strontium titanate with a superconducting film of the type Y–Ba–Cu–O deposited on its top surface. The thermostat is a copper ring with its outer circumference cooled by liquid nitrogen. The sensing element is thermally coupled with the thermostat through a thin-film thermal resistance, which serves as a regulator of the sensitivity and speed of the sensing element.

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