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Analysis of Nonstationary Heat and Mass Transfer in a Porous Catalyst Particle I*

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LIST OF SYMBOLS

$\mathbf{A}$	matrix [see Eq. (18) part two]
a	constant defining shape of particle $a = 0, 1, 2$ for slab, cylinder and sphere, respectively
D, D'	function, see Eq. (26)
h	radial mesh size
M	reciprocal value of radial mesh size
n	reaction order
K, K_1, K'_1, K_2, K'_2	constants [see Eqs. (19), (20)]
Q, Q	parameter [defined by Eq. (24) resp. (27)]
R	function [see Eq. (11) part two]
S, S'	parameter [defined by Eq. (22) resp. (28)]
$y, \bar{y}$	dimensionless concentration, mean value
Bi	Biot number
Lw	Lewis number
Nu	Nusselt number
β	parameter of heat evolution
β_1, β_n	first (nth) root of Eq. (8)
γ	parameter of activation energy
δ	Frank-Kamenetskii's parameter $\delta = \phi^2\gamma\beta$
η	function, def. by (16)
$\theta, \bar{\theta}$	dimensionless temperature, mean value
ϑ	function defined by Eq. (16)
μ	characteristic values defined by Eq. (21)
μ_1, μ_2	roots of characteristic equation (21)
ρ_1, ρ_n	first (nth) root of Eq. (7)
τ, τ'	dimensionless time
σ	constant
ϕ	Thiele modulus
φ, ψ	functions defined by Eqs. (12), (13)
$\mathbf{w}$	vector of variables [see Eq. (19) part two]

SUBSCRIPTS

B	bulk of a flowing phase
i	initial conditions
y	partial derivative with respect to y [see (17), (18)]
θ	partial derivative with respect to θ [see (17), (18)]
0	steady state
1, 2	limiting values
∞	values for approximation (29)

SUPERSCRIPTS

*	critical value

INTRODUCTION

The question of the possible number of solution of steady state mass and enthalpy balances for reaction within a porous catalyst particle has been a subject of great interest in the literature (*1–4*). Weisz and Hicks (*5*) first pointed to the fact, that three solutions are attainable. The authors of this paper show (*6*), that multiple solutions can exist only in a definite range of the value of reaction parameters. A number of authors investigated theoretically the problem of stability of individual solutions (*4*, *7–12*); some of these verified an asymptotic stability of solutions numerically on a digital computer (*7*, *11*, *12*).

The three stationary solutions (i.e., corresponding different concentration and temperature profiles within a particle) had not

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* This article may be considered to be part XIV of the series: Modelling of Chemical Reactors.

TABLE 1a
Parameters of Some Exothermic Catalytic Reactions

Reaction	γ	$\gamma\beta$	Lw	ϕ
NH_3 synthesis (*21*)	29.4	0.0018	0.00026	1.2
Synthesis of higher alcohols from CO and H_2 (*21*)	28.4	0.024	0.00020	—
Oxidation of CH_3OH to CH_2O (*21*)	16.0	0.175	0.0045	1.1
Synthesis of vinylchloride from acetylene and HCl (*21*)	6.5	1.65	0.1	0.27
Hydrogenation of ethylene (*22*)	23–27	2.7–1	0.11	0.2–2.8
Oxidation of H_2 (*25*)	6.75–7.52	0.21–2.3	0.036	0.8–2.0
Oxidation of ethylene to ethylenoxide (*21*)	13.4	1.76	0.065	0.08
Dissociation of N_2O (*23*)	22.0	1.0–2.0	—	1–5
Hydrogenation of benzene (*27*)	14–16	1.7–2.0	0.006	0.05–1.9
Oxidation of SO_2 (*21*)	14.8	0.175	0.0415	0.9

been, as far as the authors know, obtained experimentally. However, number of authors experimentally verified that important temperature gradients within the particle exist in the stationary state. Some of these measurements will be mentioned in the next chapter.

In this paper the authors make an attempt to work out such numerical procedure, which will enable one to forecast temperature gradients within the catalyst particle during the course of the transient process in such a manner, that it will not be necessary to solve complicated system of the original partial differential balance equations describing the process.

In the earlier work (*13*) it has been shown, that the relatively complicated system of partial differential equations describing nonstationary process in a porous catalyst particle can be in a certain way replaced by the system of ordinary differential equations. This simplification then enables us to perform a qualitative analysis of the process. In this paper we intend to make an analysis of a problem of stability of solution of the simplified equations by making use of methods of nonlinear mechanics. Theoretical results will then be verified on calculated examples.

II. Diffusion and Reaction in the Non-Isothermal Catalyst Particle

A. *Experimental Results*

Simultaneous heat and mass transfer inside a porous catalyst particle was the subject of great experimental activity. On the basis of the known values of the coefficients of thermal conductivity and effective diffusivity within the particle Damköhler (*19*) forecasted already in 1943 the existence of temperature gradients inside the particle, but he estimated them as small (3°C). Later on Wheeler (*20*) determined, that in the case of hydrogenation reactions the temperature difference as high as 100°C can exist inside the particle and Prater (*28*) estimated for the reaction of cyclohexan dehydrogenation that the decrease of temperature is about 50°C.

The values of parameters which appear in equations describing heat and mass transfer within a catalyst particle were summarized by Weisz and Hicks (*5*) and by Slinko, Malinovskaya and Beskov (*21*). In the next Table 1a some typical values of important parameters of reactions used in practice or in research are shown.

The important temperature differences within a particle were measured by the number of authors. So Cunningham and others (*22*) obtained temperature differences 17.5–37.4°C for the reaction of hydrogenation of ethylene, Hugo and Miller (*23*) measured the maximum temperature gradient 26°C for the reaction of N_2O dissociation, Wurzbacher (*24*) measured temperature differences 40–60°C, Maymo and Smith (*25*) the differences 8–103°C and Miller and Deans (*26*) the differences between 6.3–30°C for the reaction between hydrogen and oxygen and Irving and Butt (*27*) the temperature differences in the range 6–27°C for the reaction of benzene hydrogenation.

B. *Basic Model*

When deriving mathematical model for the description of heat and mass transfer inside a porous catalyst particle one usually assumes, that heat and mass transfer can be formally described by means of Fick and Fourier law respectively. We shall moreover deal only with the case of the simple power-law kinetics and also assume that only two components are present in the reaction mixture. Further, we shall suppose that the reaction proceeds without change in the number of moles. For the sake of generality we shall consider different component concentrations at the surface of the particle and inside the bulk of the flowing medium.

With the above given assumptions the general mass and enthalpy balances describing transient heat and mass transfer within the catalyst particle can be derived and these then can be changed into dimensionless form (*8*). Resulting partial differential equations are presented in the next chapter.

III. TRANSPORT EQUATIONS. APPROXIMATE EQUATIONS

Nonstationary heat and mass transfer process inside a porous catalyst particle can be described by the following equations (*13*)

$$Lw\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} + \frac{a}{x}\frac{\partial y}{\partial x} - \frac{\delta}{\gamma\beta}y^n \times \exp\left(\frac{\theta}{1+\theta/\gamma}\right) \quad (1)$$

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial x^2} + \frac{a}{x}\frac{\partial \theta}{\partial x} + \delta y^n \times \exp\left(\frac{\theta}{1+\theta/\gamma}\right) \quad (2)$$

with initial conditions

$$\tau = 0{:}\ \theta = \theta_i(x),\ y = y_i(x) \quad (3)$$

and boundary conditions in the form

$$\tau > 0;\ x = 1{:}\quad y = y_B - \frac{1}{Nu}\frac{\partial y}{\partial x}$$

$$\theta = \theta_B - \frac{1}{Bi}\frac{\partial \theta}{\partial x}$$

$$x = 0{:}\ \frac{\partial y}{\partial x} = \frac{\partial \theta}{\partial x} = 0. \quad (4)$$

Equations (1) and (2) can be simplified, if we substitute for the differential operator on the right hand side the algebraic expression (*13*).

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{a}{x}\frac{\partial \theta}{\partial x} \approx -\rho_1{}^2\theta \quad (5)$$

respectively

$$\frac{\partial^2 y}{\partial x^2} + \frac{a}{x}\frac{\partial y}{\partial x} \approx \beta_1{}^2(1-y) \quad (6)$$

where ρ_1 is the first root of equation

$$\begin{aligned} &\rho \operatorname{cotg} \rho + Bi = 1 && (a = 2)\\ &\rho J_1(\rho) = Bi J_0(\rho) && (a = 1)\\ &\operatorname{tg}\rho = -\rho/Bi && (a = 0) \end{aligned} \quad (7)$$

and β_1 is the first root of equation

$$\begin{aligned} &\beta \operatorname{cotg} \beta + Nu = 1 && (a = 2)\\ &\beta J_1(\beta) = Nu J_0(\beta) && (a = 1)\\ &\operatorname{tg}\beta = -\beta/Nu && (a = 0) \end{aligned} \quad (8)$$

On introducing (5) and (6) into Eqs. (1) and (2) we obtain

$$Lw\frac{dy}{d\tau} = \beta_1{}^2(1-y) - \frac{\delta}{\gamma\beta}y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right) \quad (9)$$

$$\frac{d\theta}{d\tau} = -\rho_1{}^2\theta + \delta y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right) \quad (10)$$

with initial conditions

$$\tau = 0{:}\ \theta = \theta_i,\ y = y_i \quad (11)$$

The solution of Eqs. (9)–(11) can be numerically obtained relatively more easily than that of the original system (1)–(4).

In the following part of the paper we shall consider only the case, where Nusselt and Biot numbers are equal, i.e., the case where $\beta_1 = \rho_1$. By making use of the methods of Ljapunov's analysis (*14*) we shall then discuss the questions of asymptotic stability of solution of simplified balance equations.

IV. ASYMPTOTIC STABILITY

The autonomous system (9)–(11) can be rewritten in the form:

$$\frac{d\theta}{d\tau} = \psi(y,\theta) \tag{12}$$

$$\frac{dy}{d\tau} = \varphi(y,\theta) \tag{13}$$

Steady states are then the points y_0, θ_0, that fulfill the relation

$$\psi(y_0,\theta_0) = \varphi(y_0,\theta_0) = 0 \tag{14}$$

When the dependence $\rho \sim y$ as a function of time is under consideration, it is convenient to work with a phase plane $\theta - y$ (as has been proved in the similar problem for CSTR (*15*)). In the phase plane $\theta - y$ steady states (y_0,θ_0) correspond to singular points of the differential equation

$$\frac{d\theta}{dy} = \frac{\psi(y,\theta)}{\varphi(y,\theta)} \tag{15a}$$

respectively

$$\frac{dy}{d\theta} = \frac{\varphi(y,\theta)}{\psi(y,\theta)} \tag{15b}$$

On introducing new variables

$$\begin{aligned} \eta &= y - y_0 \\ \vartheta &= \theta - \theta_0 \end{aligned} \tag{16}$$

into Eqs. (12) and (13) we obtain (when considering only the first order terms) a linearized system

$$\frac{d\eta}{d\tau} = \varphi_y\eta + \varphi_\theta\vartheta \tag{17}$$

$$\frac{d\vartheta}{d\tau} = \psi_y\eta + \psi_\theta\vartheta \tag{18}$$

Here, for instance, ψ_y denotes $\partial\psi/\partial y$ at the point $y = y_0$ and $\theta = \theta_0$. Equations (17) and (18) represent the system of two linear differential equations with constant coefficients. A general solution of the system will be in the form

$$\eta = K_1 \exp(\mu_1\tau) + K_2 \exp(\mu_2\tau) \tag{19}$$

$$\vartheta = K'_1 \exp(\mu_1\tau) + K'_2 \exp(\mu_2\tau) \tag{20}$$

where μ_1 and μ_2 are roots of the characteristic equation

$$\mu^2 - (\varphi_y + \psi_\theta)\mu + \varphi_y\psi_\theta - \varphi_\theta\psi_y = 0 \tag{21}$$

Linearized Eqs. (17) and (18) correspond to the original Eqs. (12) and (13) only in the nearest neighborhood of the point (y_0,θ_0). On the basis of knowledge of the roots μ_1 and μ_2 we can follow a character of solution of Eqs. (12) and (13) or (15a) and (15b) in the neighborhood of the steady state (y_0,θ_0). The departures η, φ from the steady state can be damped with increasing time (both roots μ_1 and μ_2 have negative real parts) or can increase (when at least one of the roots has a positive real part). In the first case we shall speak about a stable singular point of the Eqs. (15a) resp. (15b) or about an asymptotically stable solution of Eqs. (12) and (13). In the other case we then shall speak about an unstable solution.

When using Poincare's classification (*16*) we can divide singular points of Eqs. (15a) resp. (15b) in agreement with values of μ_1 and μ_2 into the points of the type of a node, focus, saddle and a centre. Since we are concerned with the linear approximation of the nonlinear problem, we shall not further consider a singular point of the type of a centre.

Let us denote

$$S = \varphi_\theta\psi_y - \varphi_y\psi_\theta \tag{22}$$

$$D = (\varphi_y - \psi_\theta)^2 + 4\varphi_\theta\psi_y \tag{23}$$

$$Q = \varphi_y + \psi_\theta \tag{24}$$

In Table 1 are then characterized the individual types of singular points.

TABLE 1
Types of Singular Points

Saddle	$S > 0$		always unstable
node	$S < 0; D \geq 0$	$Q < 0$	stable
		$Q > 0$	unstable
focus	$D < 0$	$Q < 0$	stable
		$Q > 0$	unstable

The values of partial derivatives that appear in Eqs. (17) and (18) are in our case as follows:

$$\varphi_y = \frac{\rho_1^2}{Lw}\left(n - 1 - \frac{n}{y_0}\right)$$

$$\varphi_\theta = -\frac{\rho_1^2(1 - y_0)}{Lw(1 + \theta_0/\gamma)^2}$$

$$\psi_y = \frac{n\rho_1^2\theta_0}{y_0}$$

$$\psi_\theta = \rho_1^2\left(\frac{\theta_0}{(1+\theta_0/\gamma)^2} - 1\right) \qquad (25)$$

(Here we have used Eqs. (12) and (13) where $\rho_1 = \beta_1$). The signs of expressions D, Q and S are determined by the signs of D', Q' and S':

$$D' = \left[\left(n - 1 - \frac{n}{y_0} + Lw\right)\left(1 + \frac{\theta_0}{\gamma}\right)^2 - \theta_0 Lw\right]^2 - \frac{4nLw\theta_0(1-y_0)(1+\theta_0/\gamma)^2}{y_0} \qquad (26)$$

$$Q' = \frac{n-1}{Lw} - \frac{n}{Lwy_0} - 1 + \frac{\theta_0}{(1+\theta_0/\gamma)^2} \qquad (27)$$

$$S' = \theta_0 n(y_0 - 1) - (ny_0 - y_0 - n) \times [\theta_0 - (1+\theta_0/\gamma)^2] \qquad (28)$$

As can be seen from (28), the condition of existence of a saddle is independent of value of Lw. It was shown before (*3*), when analyzing steady state transport equations for nonisothermal diffusion within a catalyst particle, that a character of solution does not change essentially if for the temperature dependence of the rate constant the following approximation is used:

$$\exp\frac{\theta}{1+\theta/\gamma} \approx \exp\theta. \qquad (29)$$

For the sake of simplicity we shall first deal with results obtained for this approximation. Expression (28) can be then rewritten into the form.

$$S' = \theta_0 y_0 + ny_0 - y_0 - n \qquad (28a)$$

For an existence of a saddle ($S' > 0$) we obtain

$$\gamma\beta > (1 + \sqrt{n})^2 \qquad (30)$$

and

$$\theta \in (\theta_1, \theta_2)$$

where

$$\theta_{1,2} = \frac{\gamma\beta + 1 - n}{2} \pm \frac{1}{2}[(\gamma\beta + 1 - n)^2 - 4\gamma\beta]^{1/2} \qquad (31)$$

It means, that if a singular point has to be that of a saddle type parameter $\gamma\beta$ must be higher than a certain critical value and simultaneously the steady state value of temperature θ_0 must lie within the limits given by Eq. (31). The steady state transport equations can have three solutions in the case where condition (30) is valid (*3*). It is known, that both upper and lower solutions are stable with regard to small perturbations imposed and that the middle one is always unstable. Numerical calculations have shown (*7, 12*), that in the lower case a reactant consumption is very small (low values of θ_0) while in the upper case reactant consumption is high and reaction takes place mostly in surface parts of a particle (high values of θ_0). Dimensionless temperature θ in a middle steady state lies always between the values θ_1 and θ_2 given by Eq. (31). The middle state is of a saddle type and is, therefore, always unstable (regardless of the value of parameter Lw).

A stability of a solution that is not of the saddle type is determined by the condition $Q' < 0$. When approximation (29) is used, this condition can be written in the form

$$\frac{n-1}{Lw} - \frac{n}{Lwy_0} + \theta_0 - 1 < 0 \qquad (32a)$$

The condition will be fulfilled always, when

$$\theta_0 < 1. \qquad (32)$$

The stability of solution is then independent of the value of parameter Lw. If condition (32) is not fulfilled, then it is necessary for stability to hold:

$$Lw < Lw_\infty^* = \frac{\frac{n}{y_0} + 1 - n}{\theta_0 - 1} \qquad (33)$$

i.e., the value of Lewis number has to be lower than certain critical value, Lw_∞^*. For $Lw > Lw_\infty^*$ the steady state is unstable.

From the condition, which determines an existence of focus, we obtain that in this case the Lewis number must be in the interval

$$Lw \in (Lw_{\infty 1}, Lw_{\infty 2}) \qquad (34)$$

where $Lw_{\infty 1}$ and $Lw_{\infty 2}$ are determined as

TABLE 2

CLASSIFICATION OF REGIONS OF STABILITY. APPROXIMATION (29), $n = 1$

$\gamma\beta$	ϕ	Number of steady states	θ_0	Stability
$\gamma\beta \leq 1$	—	1	$(\theta_0 < 1)$	stable
$1 < \gamma\beta \leq (\gamma\beta)^*$	—	1	$\theta_0 \leq 1$	stable
			$\theta_0 > 1$	stable for $Lw < Lw_\infty^*$
$\gamma\beta > (\gamma\beta)^*$	$\phi < \phi_1$	1	$\theta_0 \leq 1$ $\theta_0 > 1$	stable stable for $Lw < Lw_\infty^*$
	$\phi_1 < \phi < \phi_2$	3	lower state $\theta_0 \leq 1$ $\theta_0 > 1$	 stable stable for $Lw < Lw_\infty^*$
			middle state	always unstable (saddle)
			upper state $(\theta_0 > 1)$	stable for $Lw < Lw_\infty^*$
	$\phi > \phi_2$	1	$(\theta_0 > 1)$	stable for $Lw < Lw_\infty^*$

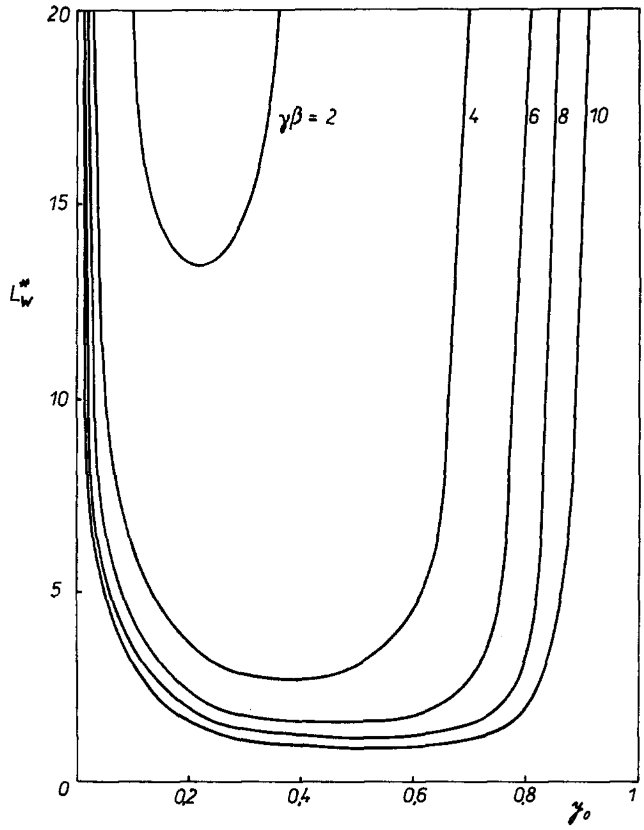

FIG. 1. Dependence of Lw^* on $y_0, \gamma = 20$.

$$Lw_{\infty 1,2} = \frac{1}{y_0(1-\theta_0)^2}\Big\{n(1+\theta_0) - y_0(n-1) - y_0\theta_0(n+1) \pm 2\sqrt{n\theta_0(1-y_0)[n - y_0(n-1) - y_0\theta_0]}\Big\} \tag{35}$$

The expression under root symbol is positive for values of $\theta_0 \notin \langle\theta_1,\theta_2\rangle$; that is in agreement with the condition of nonexistence of a saddle. A stationary point that has not a character of a saddle will have the character of a focus if condition (34) will be fulfilled and of a node if this condition will not be fulfilled. The stability of a focus or a node is determined by relations (32) and (33). A survey of regions of stability for a first order reaction is given in Table 2.

In none of the criteria given above we have met with the parameter ρ_1 (which characterizes a geometry of a catalyst particle and heat and mass transfer at the outer surface of the particle). The value of parameter ρ_1 is, however, contained in an implicit way in dimensionless values of concentration and temperature at the steady state $-y_0$ and θ_0. In the case where approximation (29) is not considered the picture does not vary qualitatively. For the condition of stability ($Q' < 0$) conditions similar to relations (32) and (33) are obtained:

$$\theta_0 \leq \left(1 + \frac{\theta_0}{\gamma}\right)^2 \tag{32'}$$

$$Lw < Lw^* = \frac{\dfrac{n}{y_0} + 1 - n}{\dfrac{\theta_0}{(1+\theta_0/\gamma)^2} - 1} \tag{33'}$$

Relation (33′) is for a first order reaction shown in Fig. 1 ($\gamma = 20$) and Fig. 2 ($\gamma = 40$). The critical value of Lewis number Lw^* is here given as a function of dimensionless concentration at the steady state $-y_0$. It

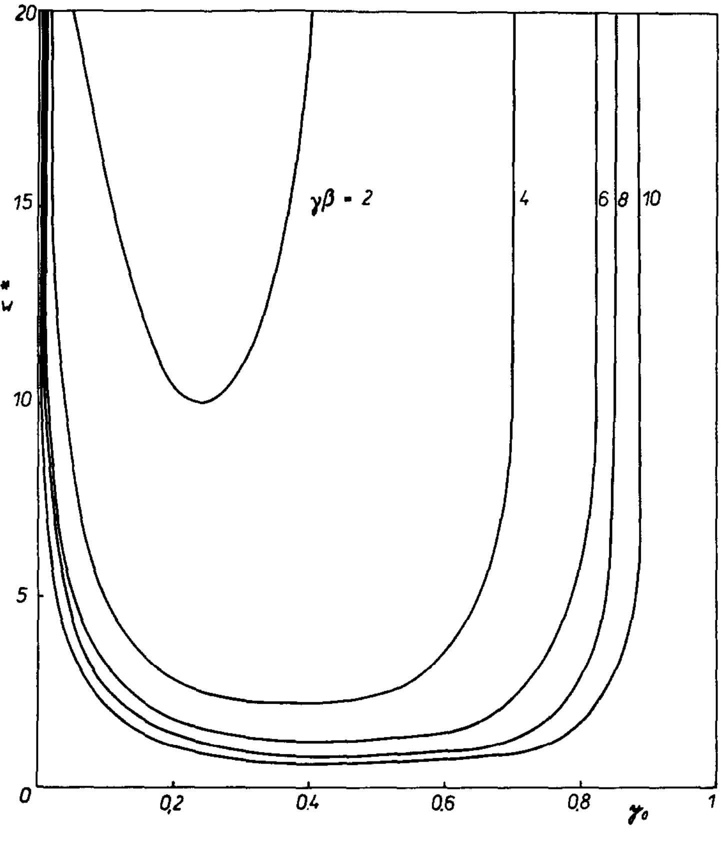

FIG. 2. Dependence of Lw^* on $y_0, \gamma = 40$.

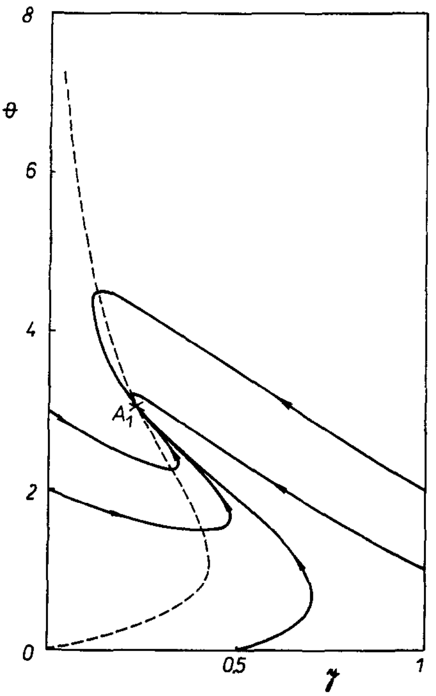

FIG. 3. Trajectories in the phase plane, $Lw = 1$. Parameters see Table 3.

follows from the figures, that with increasing value of $\gamma\beta$ the value of Lw^* decreases. But in the wide range of values of y_0 (and therefore also the values of Thiele modulus ϕ) the value of Lw^* is approximately the same. Lower values of y_0 (higher values of ϕ) correspond to a case of high reactant consumption, when a reaction takes place predominantly in the surface parts of a catalyst and concentration very quickly decreases to zero value (7) towards the center of the particle. In this working regime of a catalyst the value of critical Lewis number again increases. For high values of y_0 condition (32′) is fulfilled and the process is always stable.

For an existence of a focus conditions similar to those given by relations (34) and (35) can be derived:

$$Lw \in (Lw_1, Lw_2) \qquad (34')$$

where $Lw_{1,2}$ are the roots of the quadratic equation

$$ALw^2 + BLw + C = 0 \qquad (35')$$

where

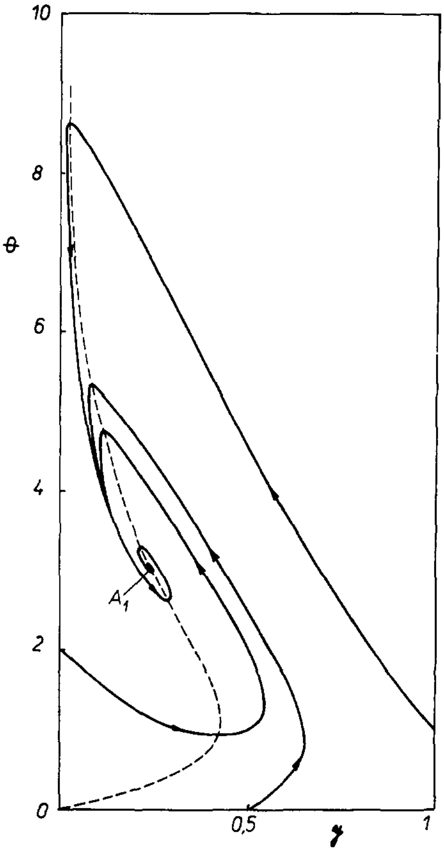

FIG. 4. Trajectories in the phase plane, $Lw = 2.5$. Parameters see Table 3.

$$A = \left[\left(1 + \frac{\theta_0}{\gamma}\right)^2 - \theta_0\right]^2$$

$$B = 2\left(n - 1 - \frac{n}{y_0}\right)\left(1 + \frac{\theta_0}{\gamma}\right)^2 \times \left[\left(1 + \frac{\theta_0}{\gamma}\right)^2 - \theta_0\right] - 4n\theta_0\left(1 + \frac{\theta_0}{\gamma}\right)^2 \times \frac{1 - y_0}{y_0}$$

$$C = \left(n - 1 - \frac{n}{y_0}\right)^2\left(1 + \frac{\theta_0}{\gamma}\right)^4$$

Conditions analogous to those of (30)–(31) for existence of a solution of the type of a saddle are more complicated for the case where approximation (29) is not valid and analytical criteria in explicit form cannot be simply obtained. For given values of parameters can be, for example, values of θ_1 and θ_2 evaluated from an algebraic equation of a higher degree (condition $S' = 0$) numerically.

V. Description of Numerical Results

The above given qualitative analysis is valid only in the neighborhood of a steady state. When we wish to follow a course of solution in time we have to integrate Eqs. (9) and (10) numerically. For a numerical integration the method of Runge–Kutta–Merson with automatic control of integration step size was used. The results obtained for different initial conditions θ_i, y_i are graphically shown in the phase plane $\theta - y$. We shall deal with a discussion of results for both cases, i.e., those where only a single solution of steady state transport equations exists and also those, where there are three such solutions (*6*).

For the case, where only single solution of Eqs. (9) and (10) exists, the chosen parameters are given in Table 3. For these parameters the effect of change of Lewis number was followed.

TABLE 3

$\gamma = 20$	$n = 1$	$y_0 = 0.237$
$\beta = 0.2$	$a = 2$	$\theta_0 = 3.253$
$\delta = 9$	$Nu = Bi \to \infty$	

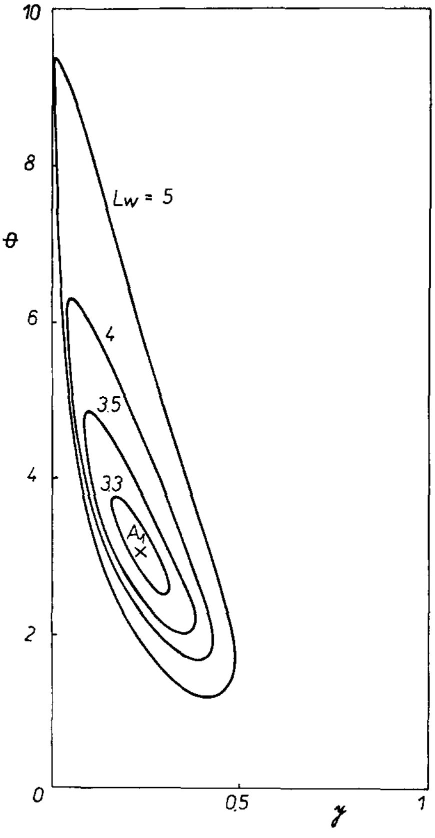

FIG. 5. Limit cycles for different values of Lewis number.

In Fig. 3 the case where $Lw = 1$[†] is shown. The single steady state $\theta_0 = 3.253$, $y_0 = 0.237$ is of a node type. The dashed line denotes the points of temperature maxima on trajectories in the phase plane. As can be seen from the figure, temperature within a catalyst particle can exceed the maximum steady state value given by Prater's relation (here $\theta = \gamma\beta = 4$). From the values of parameters given in Table 3 we can calculate the values of limits of Lewis number: Lw_1, Lw_2 and Lw^*. We obtain $Lw_1 = 1.056$; $Lw_2 = 10.02$; $Lw^* = 3.25$. When the Lewis number increases, we obtain successively the following cases (Table 4).

TABLE 4

Lw	Type of stationary point	Stability
0–1.056	node	stable
1.056–3.25	focus	
3.25–10.02	focus	unstable
10.02–∞	node	

The cases given in Table 4 are shown in figures. In Fig. 4 ($Lw = 2.5$) is presented the case, where the stationary point is of the type of a stable focus. If the value of Lw exceeds the critical value Lw^*, a limit cycle arises. This limit cycle is stable from both sides. In Fig. 5 are shown limit cycles for various values of Lewis number. With

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[†] When introducing substitution $\tau = \sigma^2\tau'$ and at the same time $\phi = \sigma\phi$, $\phi'_1 = \sigma\rho_1$ into Eqs. (9) and (10), results in a phase plane will not change. Figure 3, therefore, corresponds not only to the values $\rho_1 = 3.1416$, $\phi = 1.5$, but also for instance to the values $\rho'_1 = 1.5708$ ($a = 0$) and $\phi' = 0.75$. Numerical analysis can thus be made only for one value of the parameter ρ_1 and for a succession of values of the parameter ϕ.

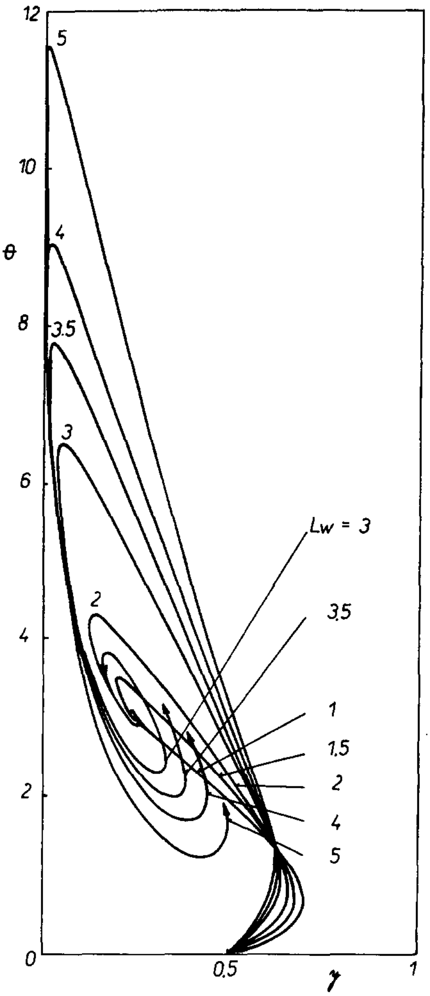

FIG. 6. Effect of Lewis number on maximum attained temperature inside a particle.

increasing value of Lewis number the limit cycles also increase and, in agreement with the results of Aris and Amundson for a CSTR (*15*), their asymmetry enlarge. The condition for unstability is, therefore, also the condition for existence of a limit cycle (and also of existence of a stationary periodic process). So in the case of a single steady state there exist only the following cases of stationary states: a stable node or focus and a limit cycle.

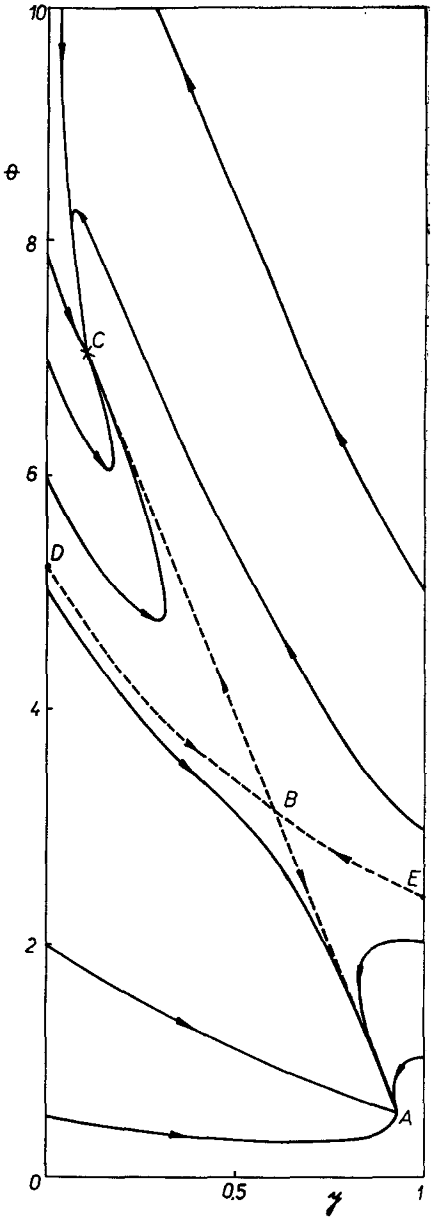

FIG. 7. Trajectories in the phase plane, $Lw = 1$. Parameters see Table 5.

The maximum value of temperature attainable inside a catalyst particle during a transient process is, as has been shown by Wei (*17*) a function of Lewis number and depends also on values of θ_i and y_i. The dependence is illustrated in Fig. 6, where integral curves, starting from one initial point, are presented for different values of Lewis number.

Now we shall deal with the case where three steady states exist. The parameters are listed in Table 5.

As well as in the foregoing example we shall follow the effect of variation of Lewis

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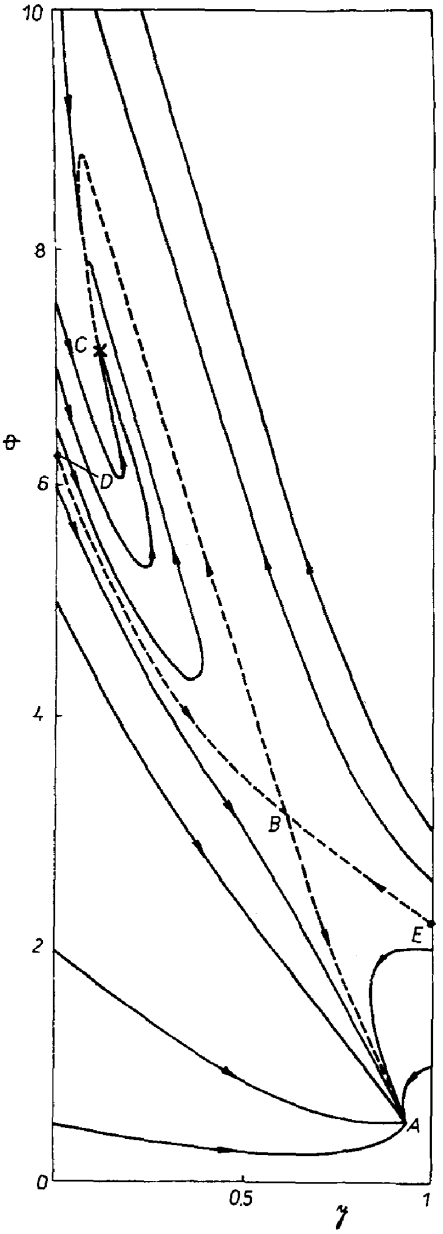

FIG. 8. Trajectories in the phase plane, Lw = 1.5. Parameters see Table 5.

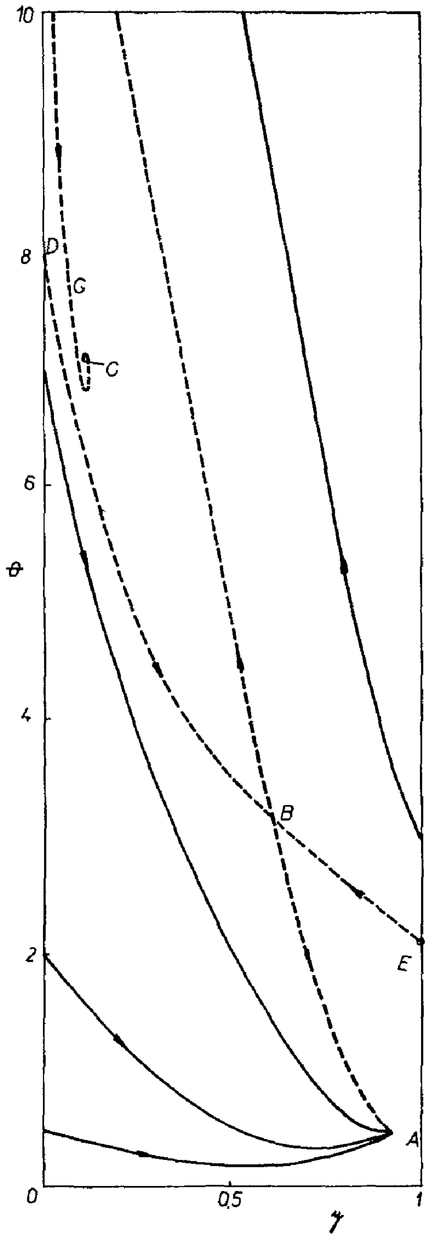

FIG. 9. Trajectories in the phase plane, Lw = 2.5. Parameters see Table 5.

TABLE 5

		A	B	C
$\gamma = 20$	$n = 1$	$y_0 = 0.932$;	0.607;	0.108
$\beta = 0.4$	$a = 2$	$\theta_0 = 0.544$;	3.144;	7.914
$\delta = 3.38$	$Nu = Bi \rightarrow \infty$			

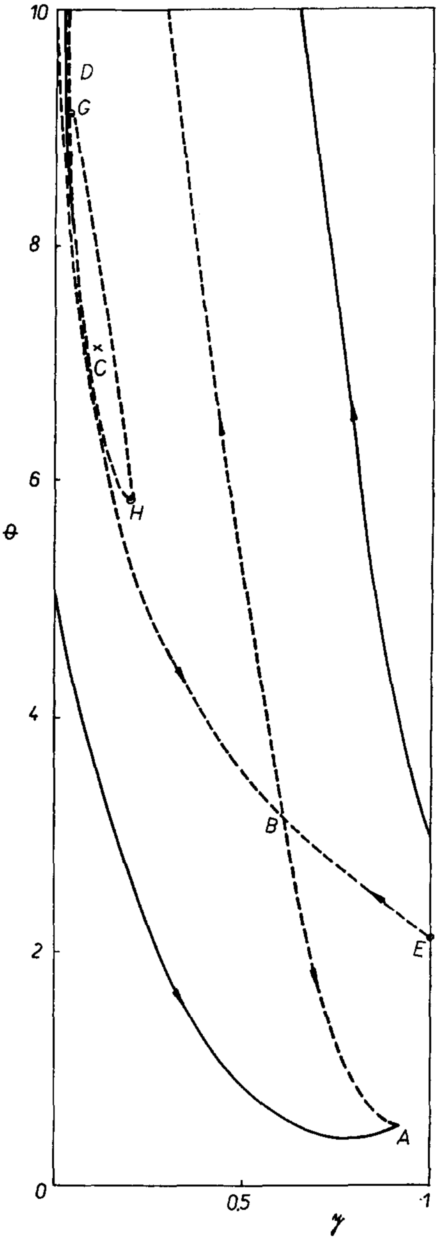

FIG. 10. Trajectories in the phase plane, $Lw = 3.3$. Parameters see Table 5.

number. The coordinates of the steady states in the phase plane are given in Table 5. The lower steady state A is always stable as the condition (32′) is fulfilled. For the upper steady state C we obtain from (33′) $Lw^* = 3.21$. Trajectories $y - \theta$ for $Lw = 1$ are given in Fig. 7. The steady states A and C are stable, the state B is unstable (a saddle).

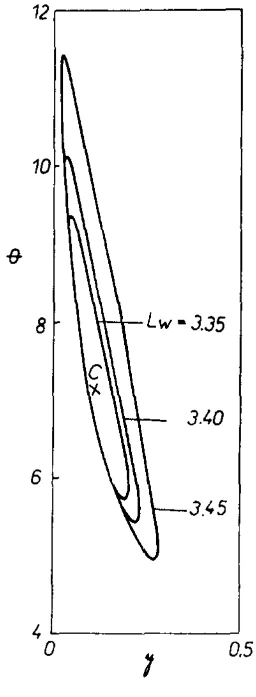

FIG. 11. Limit cycles for different values of Lewis number.

Separatrix DBE divides integral curves according to appurtenance to the steady states A or C. Integral curves BC and BA are straight lines. A similar situation is shown in Fig. 8, where $Lw = 1.5$. Separatrix DBE is turned with regards to the foregoing example and the integral lines BA and BC are not straight lines. In Fig. 9 the picture for $Lw = 2.5$ is presented. The upper steady state C is of a focus type. The trajectories $y - \theta$ starting in the region EBF make a circuit around the integral curve BFGC, connecting the steady states B and C, and must go between D and G. When Lewis number exceeds Lw^* the upper steady state becomes unstable. The case where $Lw = 3.3$ is shown in Fig. 10. Around the upper steady state is formed a limit cycle. The branch DB of separatrix does not cease yet, but intermingles to the limit cycle. All the trajectories starting in the region EBF must go through a narrow gap between the two lines. The dependence of a shape of the limit cycle on Lewis number is shown in Fig. 12. When Lewis number further increases, the limit cycle around the steady state C vanishes. The only steady state A then exists and all the trajectories in the phase plane go towards it. The trajectories starting in the region BDFG of the phase plane must go between the points G and C. The trajectories starting in the region EBD go around the curve BDF from the outer side.

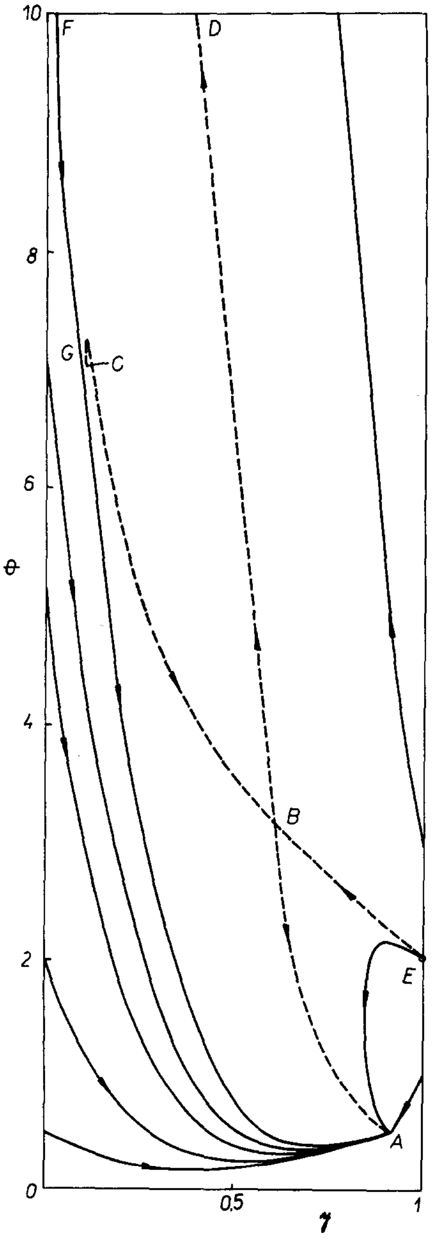

FIG. 12. Trajectories in the phase plane, $Lw = 5$. Parameters see Table 5.

We have discussed above the example with three steady states, from which the lower one fulfills the condition (32′) and is, therefore, always stable. But for the problems with three solutions there usually exists a small range of parameters ϕ closely below the value ϕ_2, where the condition (32′) is not fulfilled. Then the value of Lw can be chosen in such a manner, that also the lower steady state becomes unstable. Such a case can be realized if the value of δ in Table 5 is changed for $\delta = 4.476$. The corresponding value of θ_0 is then equal to 1.165 and Lw^* equals 28.9. A numerical simulation has shown, that the limit cycle which arises is numerically evaluated with difficulties and for higher values of Lw can include all three steady states.

APPENDIX

Stability of Solution of Eqs. (1) and (2) for a Zero Order Reaction

For a zero reaction there is no coupling between mass and enthalpy balances and the equations can be, therefore, solved successively. For qualitative analysis it will suffice, when we shall discuss only enthalpy balance. It is for a zero order reaction in the form

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial x^2} + \frac{a}{x}\frac{\partial \theta}{\partial x} + \delta \exp\left(\frac{\theta}{1 + \theta/\gamma}\right) \qquad (2')$$

On introducing approximation (5) we obtain

$$\frac{d\theta}{d\tau} = -a_1^2\theta + \delta \exp\left(\frac{\theta}{1 + \theta/\gamma}\right) \qquad (10')$$

The linearized equation is in the form

$$\frac{d\vartheta}{d\tau} = \vartheta\left[\frac{\delta}{(1 + \theta_0/\gamma)^2} \times \exp\left(\frac{\theta_0}{1 + \theta_0/\gamma}\right) - a_1^2\right] \qquad (18')$$

From the steady state solution (when in (10′) is $d\theta/d\tau = 0$) we obtain the expression for a_1^2. If this is substituted into (18′) we obtain

$$\frac{d\vartheta}{d\tau} = \vartheta\delta \exp\left(\frac{\theta_0}{1 + \theta_0/\gamma}\right) \times \left[\frac{1}{(1 + \theta_0/\gamma)^2} - \frac{1}{\theta_0}\right] \qquad (18'')$$

Solution of Eq. (18″) is in the form

$$\vartheta = \vartheta_i \exp K\tau$$

where a sign of K is determined by a sign of expression $[1/(1+\theta_0/\gamma)^2 - 1/\theta_0]$. When $\gamma \to \infty$ the known condition for stability $\theta_0 < 1$[18] is obtained. For bounded values of γ the solution is unstable in the range of values of θ_0, given by the expression

$$(\theta_0)_{1,2} = \gamma\left(\gamma/2 - 1 \pm \sqrt{\frac{\gamma^2}{4} - \gamma}\right). \qquad (31')$$

As follows from Eq. (31′) the solution is always stable for $\gamma < 4$.

Stability of Solution of Eqs. (1) and (2) for an Isothermal Reaction

In an isothermal case we can consider only Eq. (1) which is in the form

$$Lw\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} + \frac{a}{x}\frac{\partial y}{\partial x} - \frac{\delta}{\gamma\beta}y^n. \qquad (1')$$

On introducing approximation (6) we obtain

$$Lw\frac{dy}{d\tau} = \beta_1^2(1-y) - \frac{\delta}{\gamma\beta}y^n \qquad (9')$$

The linearized Eq. (17) is then in the form

$$\frac{d\eta}{d\tau} = -\frac{1}{Lw}(\beta_1^2 + n\phi^2 y_0^{n-1})\eta$$

Therefore it holds

$$\eta = K_1 \exp\left[-\frac{1}{Lw}(\beta_1^2 + n\phi^2 y_0^{n-1})\right]\tau \qquad (19')$$

From (19′) it follows, that the steady state of the isothermal problem (9′) is always stable.

SUMMARY

An analysis of transient heat and mass transfer within a porous catalyst particle has been made on the basis of an approximate model, that consists of two nonlinear ordinary differential equations. Classification of solutions of equations in the neighborhood of steady states and a discussion of questions of stability was performed on the basis of the first method of Ljapunov. Conclusions on the stability of given steady states are expressed in the form of analytic criteria. cally solved examples. A possibility of existence of limit cycle is proved and discussed for unstable cases.

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