EFFECT OF INTERNAL DIFFUSION ON CATALYTIC REACTIONS. X.*
INTRAPARTICLE INSTABILITIES UNDER NEARLY REALISTIC CONDITIONS

P. MITSCHKA and P. SCHNEIDER

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol

Received June 14th, 1971

Results of the stability analysis of a catalytic reaction with nonisothermal diffusion and with a simple kinetic equation of the Langmuir–Hinshelwood type (*1*) were used for determining minimum values of the critical Lewis number Lw**. The possibility is discussed of their further possible lowering by including other factors.

Among results of the stability analyses of the behaviour of a porous catalyst particle inside which an exothermic catalytic reaction of the first order with respect to the reactant takes place, there was a finding that undamped concentration and temperature oscillations could arise only at considerably high values of the Lewis number[1-3]. Such high values are not realistic for catalytic systems known so far[1]. Even the inclusion of further effects as for example of the external heat and mass transfer and of the change in the number of moles during a catalytic reaction[4] did not result in a substantial lowering of critical values of the number. It was found[5] on the other hand that instabilities of this type can arise even at isothermal conditions if a bimolecular catalytic reaction is described by a kinetic equation rendering possible a decrease in the reaction rate with increasing concentration (*e.g.* some equations of the Langmuir–Hinshelwood type).

Hence, a possibility arises of analysing the stability in a case tending towards the instability from the reasons of both the reaction being exothermic and the concentration dependence of the reaction rate. However, as the case of a nonisothermal bimolecular reaction is described by a system of at least three partial differential equations whose stability analysis is very difficult, we shall limit ourselves to a simpler case of a monomolecular exothermic reaction with a kinetic equation for the so called "dual site" mechanisms according to the Langmuir–Hinshelwood classification. With this kinetic equation, pure concentration-type instabilities are possible even in an isothermal case[6].

Basic relations. By the method employed for example in previous works[5,6], the nonisothermal nonstationary internal diffusion accompanied by a catalytic reaction A → products obeying a simple rate equation of the Langmuir–Hinshelwood type (*1*)

---

* Part IX: This Journal *37*, 196 (1972).

$$R_A = k(T)\, K_A c_A/(1 + K_A c_A)^2 \tag{1}$$

can be described for a catalyst particle in the form of an infinite slab of the width $2L$ by a system of two partial differential equations (*2*) – (*3*):

$$\frac{\partial y}{\partial \tau} = \frac{\partial^2 y}{\partial x^2} - M_L^2 \frac{y(1 + B)^2}{(1 + By)^2} \exp\left[\frac{\Theta}{(1 + \Theta/\gamma)}\right], \tag{2}$$

$$\frac{1}{Lw}\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial x^2} + \beta\gamma M_L^2 \frac{y(1 + B)^2}{(1 + By)^2} \exp\left[\frac{\Theta}{(1 + \Theta/\gamma)}\right], \tag{3}$$

with boundary conditions

$$x = 0 : \partial y/\partial x = \partial \Theta/\partial x = 0\,; \quad x = 1 : y = 1, \quad \Theta = 0\,. \tag{3a}$$

The dimensionless variables and parameters are given by relations (*4*):

$$\begin{gathered} y \equiv c_A/c_{Ai} \quad \Theta \equiv (T - T_i)\,\gamma/T_i \quad x \equiv z/L \quad \tau \equiv D_A t/L^2\,, \\ M_L \equiv L\sqrt{[R_A(y = 1)/D_A c_{Ai}]} \quad B \equiv K_A c_{Ai} \quad Lw \equiv \lambda/D_A \varrho c_p = a/D_A\,, \\ \beta \equiv (-\Delta H)\, D_A c_{Ai}/\lambda T_i \quad \gamma \equiv E/RT_i\,. \end{gathered} \tag{4}$$

By using the linearisation principle according to Hlaváček, Kubíček and Marek[1,4,5,7], the system of Eqs (*2*)–(*3*) can be transformed into two ordinary differential Eqs (*5*), (*6*) for suitable (*e.g.* mean) values of the dimensionless concentration and temperature $\bar{y}, \overline{\Theta}$

$$\frac{d\bar{y}}{d\tau} = \left(\frac{\pi}{2}\right)^2 (1 - \bar{y}) - M_L^2 \frac{\bar{y}(1 + B)^2}{(1 + B\bar{y})^2} \exp\left[\frac{\overline{\Theta}}{(1 + \overline{\Theta}/\gamma)}\right], \tag{5}$$

$$\frac{1}{Lw}\frac{d\overline{\Theta}}{d\tau} = -\left(\frac{\pi}{2}\right)^2 \overline{\Theta} + \beta\gamma M_L^2 \frac{\bar{y}(1 + B)^2}{(1 + B\bar{y})^2} \exp\left[\frac{\overline{\Theta}}{(1 + \overline{\Theta}/\gamma)}\right], \tag{6}$$

with an initial condition

$$\tau = 0\,, \quad \bar{y} = \bar{y}_0\,, \quad \overline{\Theta} = \overline{\Theta}\,. \tag{7}$$

The system of Eqs (*5*)–(*6*) can be analysed by the first Ljapunov method for the asymptotic stability of singular points by the method described in a previous work[5]. The quantities S and Q determining the character of separate singular points in the sense of the Poincaré classification are given by the expressions

$$S \equiv \bar{y}_s(1 + B\bar{y}_s)\,[\overline{\Theta}_s - (1 + \overline{\Theta}_s/\gamma)^2] - (1 - \bar{y}_s)(1 - B\bar{y}_s)(1 + \overline{\Theta}_s/\gamma)^2\,, \tag{8}$$

$$Q \equiv \mathrm{Lw}\left[\frac{\overline{\Theta}_s}{(1+\overline{\Theta}_s/\gamma)^2} - 1\right] - \left[1 + \frac{(1-\bar{y}_s)(1-B\bar{y}_s)}{\bar{y}_s(1+B\bar{y}_s)}\right], \tag{9}$$

where Prater's relation[8] (*10*) holds between the quantities $\bar{y}_s$ and $\overline{\Theta}_s$ in the stationary case (index s)

$$\overline{\Theta}_s = \beta\gamma(1-\bar{y}_s)\,. \tag{10}$$

The value of $\bar{y}_s[\bar{y}_s \in (0, 1)]$ may be determined by solving the equation describing the stationary process, which can be derived from relations (*5*) and (*6*) by setting their l.h.s. equal to zero

$$\left(\frac{\pi}{2}\right)^2 (1-\bar{y}_s) = M_L^2\,\frac{\bar{y}_s(1+B)^2}{(1+B\bar{y}_s)^2}\exp\left[\frac{\beta\gamma(1-\bar{y}_s)}{1+\beta(1-\bar{y}_s)}\right]. \tag{11}$$

The effectiveness factor in the stationary case is then

$$\bar{\eta}_s = \frac{\bar{y}_s(1+B)^2}{(1+B\bar{y}_s)^2}\exp\left[\frac{\beta\gamma(1-\bar{y}_s)}{1+\beta(1-\bar{y}_s)}\right]. \tag{12}$$

Multiplicity of the solution for the stationary case. As it was shown several times[1,5], the condition of the boundary of saddle singular solutions $S = 0$ is at the same time a condition determining the boundary between regions of unique or multiple solutions of the stationary problem. From this condition, the so called critical values of the adsorption parameter B^* may be obtained for given values of β and γ parameters such that the stationary problem has only one solution for $B < B^*$. The $B^*(\beta, \gamma)$ dependence is depicted in Fig. 1; a limiting value of $B^* = 8$ for the isothermal case ($\beta\gamma = 0$) agrees well with previous results[9]. From this figure, we can see that with increasing thermal effects of the reaction (increasing $\beta\gamma$), the value of the critical parameter B^* decreases.

Stability analysis of singular points. In the stability analysis of the system of two coupled ordinary differential Eqs (*5*)–(*6*), we shall limit ourselves only to the analysis of the stability condition of non-saddle singular points. Non-saddle points ($S < 0$) are asymptotically stable for $Q < 0$, *i.e.* if it holds

$$\mathrm{Lw}\left\{\frac{\beta\gamma(1-\bar{y}_s)}{[1+\beta(1-\bar{y}_s)]^2} - 1\right\} - \left[1 + \frac{(1-\bar{y}_s)(1-B\bar{y}_s)}{\bar{y}_s(1+B\bar{y}_s)}\right] < 0\,. \tag{13}$$

For positive values of the Lewis number, which only have a sense, and for

$$\{\beta\gamma(1-\bar{y}_s)/[1+\beta(1-\bar{y}_s)]^2\} - 1 > 0\,, \tag{14}$$

condition (*13*) may be rearranged to the form

$$\mathrm{Lw} < \mathrm{Lw}^*\,. \tag{15}$$

For Lw > 0 and for

$$\{\beta\gamma(1 - \bar{y}_s)/[1 + \beta(1 - \bar{y}_s)]^2\} - 1 < 0\,, \tag{16}$$

the non-saddle points are always stable.

The critical value of the Lewis number Lw* is defined by Eq. (*17*):

$$\mathrm{Lw}^* \equiv \frac{1 + [(1 - \bar{y}_s)(1 - B\bar{y}_s)]/[\bar{y}_s(1 + B\bar{y}_s)]}{\{\beta\gamma(1 - \bar{y}_s)/[1 + \beta(1 - \bar{y}_s)]^2\} - 1}\,. \tag{17}$$

When applying the derived criteria, it is necessary to know the region of $\bar{y}_s$ values, in which non-saddle type singular points are lying. This region may be determined by solving the relation $S = 0$ (Eq. (*8*)); the solution obtained also limits the region of multiple-valued stationary solutions. One of a possible situation is depicted schematically in Fig. 2, where besides the curve $\mathrm{Lw}^*(\bar{y}_s)$, the dependence $M_L = M_L(\bar{y}_s)$ is plotted according to Eq. (*11*).

The $\mathrm{Lw}^* - \bar{y}_s$ plane splits into existence regions of solutions with saddle (vertical band denoted by S) and non-saddle (denoted by N) character; simultaneously, the region of unique solutions of the function $\bar{y}_s(M_L)$ is shown (denotes by U) as well as

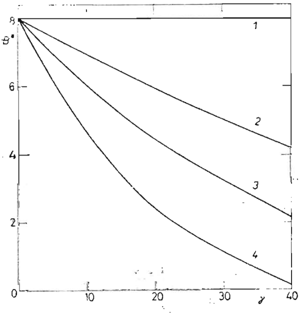

FIG. 1

Dependence of the Critical Value of the Parameter B^* on Parameters β and γ

1 β 0, *2* β 0·025, *3* β 0·05, *4* β 0·1.

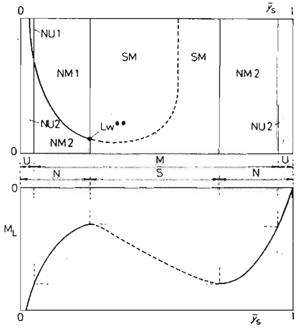

FIG. 2

Schematical Dependences of Lw* and M_L on the Mean Concentration $\bar{y}_s$ for a Constant Set of Parameters B, β, and γ

N Region of non-saddle type solutions, S region of saddle type solutions, U region of unique solutions, M region where the function $\bar{y}_s(M_L)$ is multiplevalued.

the multiplicity region (denoted by M). The curve $Lw^*(\bar{y}_s)$ separates further these regions into parts NU1, NU2, NM1, NM2 and SM.* In the SM region, there are only saddle points which are always unstable; in the NU2 part, non-saddle points exist which represent always stable unique solutions. Solutions in the NM1 and NM2 regions represent one of multiple solutions; this solution is stable in the NM2 region and unstable in the NM1 region. As points in the NU1 part form the only possible unstable solution, limiting cycles arise in this case according to Bendixon's theorem[10] (the system becomes stabilized in a state of undamped oscillations of both the mean concentration and mean temperature around the $\bar{y}_s$, $\bar{\Theta}_s$ singular point).

An unstable solution of the non-saddle type is thus possible only in the NU1 and NM1 regions; hence, the possibility of an instability occurrence depends on the value of the lowest Lewis number Lw^{**} which is determined by the intersection of the $Lw^*(\bar{y}_s)$ curve with the boundary of the non-saddle points region. This is clearly visible in Fig. 3, where dependences are plotted of the critical Lewis number on $\bar{y}_s$ for several values of the B parameter and for constant values of parameters β and γ. The part of the $Lw^*(\bar{y}_s)$ curve lying in the non-saddle solution region is shown as full, while that lying in the saddle point region as dashed. As regards the case with an unique solution (curve *1* in Fig. 3), the Lw^{**} value is given by the coordinate of the minimum of the $Lw^*(\bar{y}_s)$ curve.

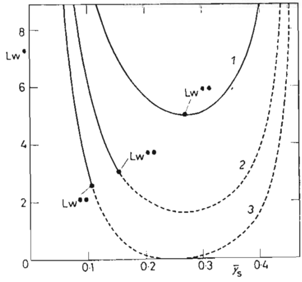

FIG. 3

Dependence of the Critical Lewis Number Lw^* on $\bar{y}_s$

β 0·05, γ 40, *1* B 2, *2* B 5, *3* B 8. The region of saddle type solutions is dashed.

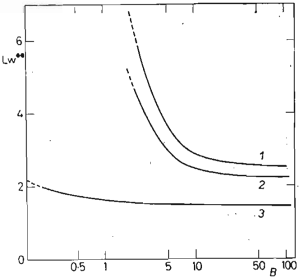

FIG. 4

Dependence of the Lowest Lewis Number Lw^{**} on the Parameter B

1 β 0·1, γ 40, *2* β 0·05, γ 40, *3* β 0·1, γ 20.

---

* Vertical asymptotes of the $Lw^*(\bar{y}_s)$ curve pass through the $\bar{y}_s = 0$ point and through a point $\bar{y}_s$ which is the solution of an equation separating the regions described by relations (*14*) and (*16*).

Minimum values of the Lewis number Lw**. As it is seen in Fig. 3, the Lw** value decreases with increasing B; adsorption effects thus shift the instability region towards lower, *i.e.* more realistic values. The B-Lw** dependence may be constructed also by simultaneous numerical solving Eq. (*17*) with the conditions $S = 0$ (Eq. (*8*)); this condition determines the geometrical locus of the so called bifurcation points, *i.e.* of points for which the $\bar{y}_s(M_L)$ dependence just branches. The obtained dependence of Lw** on the B parameter is depicted for constant β, γ pairs in Fig. 4. The existence region of unique solutions for a given B, β, γ set is dashed.

For a B parameter growing to infinity, the curves in Fig. 4 approach the lowest (asymptotic) value which, for $\beta\gamma/(1 + \beta)^2 > 1$ (*cf.* (*14*)), may be determined from relation (*18*)

$$\lim_{B \to \infty} \mathrm{Lw}^{**} = 1 + \left[\frac{\beta\gamma}{(1 + \beta)^2} - 1\right]^{-1} \qquad (18)$$

(Table I). (For $\beta\gamma/(1 + \beta)^2 < 1$, the non-saddle solutions are always stable). It follows from relation (*18*) that the lowest value of the critical Lewis number Lw** which may be reached for very strong temperature and adsorption effects of the reaction (high values of B, β, γ), equals unity. Even such magnitudes of the Lewis number are unrealistic for common catalytic processes[1]. It is however substantial that for a nonisothermal process, a lowering of critical Lewis numbers towards a value of Lw** ~ 1 was accomplished by a single factor, *i.e.* by the form of the employed kinetic equation of the Langmuir–Hinshelwood type. For the case of an exothermic reaction with power-law kinetics[4], it was necessary for reaching minimum values of critical Lewis numbers Lw** equal to several units to consider besides a nonisothermal reaction in the porous particle still other factors (heat and mass transfer inside the particle and effects caused by changes in the number of mol during the reaction)[4]. Thus, the inclusion of these and similar other effects into a Langmuir–Hinshelwood kinetics model could lower the critical Lewis numbers Lw** still further, eventually down to values which would be realistic in some catalytic processes (*e.g.* Lw ~0·11 for the ethylene hydrogenation[1]). It seems further that the minimum critical Lewis number would approach the region of realistic values the

TABLE I

Limiting Values of Lw** for $B \to \infty$

β	0·05	0·05	0·10	0·10	0·10	0·20	0·20	0·20
γ	30	40	20	30	40	20	30	40
$\mathrm{Lw}^{**}_{\mathrm{lim}}$	3·77	2·23	2·53	1·68	1·43	1·71	1·32	1·24

most by including the external heat and mass transfer, the effect of the change of the mol numbers during the reaction and primarily by including the simultaneous diffusion of two reactants[5] during an exothermic reaction.

The approximative linearisation procedure[1,4,5,7] used for a replacement of the system of partial differential Eqs *(2)*—*(3)* by the system of ordinary differential Eqs *(5)*—*(6)* loads the results obtained with some uncertainty. In number of cases it was, however, found[4,7,11] that the results concerning stability obtained by this method are in very good agreement with results obtained by solving the non-simplified problems.

LIST OF SYMBOLS

a	thermal conductivity
A	reactant
B	parameter, Eq. *(4)*
c_A	concentration of component A
c_p	specific heat of catalyst particle
D_A	effective diffusion coefficient of component A
E	activation energy of reaction
ΔH	reaction heat
k	rate constant of catalytic reaction
K_A	adsorption coefficient of component A
L	half-width of catalyst slab
Lw	Lewis number, Eq. *(4)*
Lw*	critical value of Lewis number, Eq. *(17)*
Lw**	lowest value of critical Lewis number in the region of nonsaddle solutions
M_L	diffusion modulus, Eq. *(4)*
R_A	reaction rate
R	gas constant
t	time
T	absolute temperature
x	dimensionless coordinate, Eq. *(4)*
y	dimensionless concentration, Eq. *(4)*
$\bar{y}$	mean dimensionless concentration of component A
z	length coordinate
β	parameter, Eq. *(4)*
γ	parameter, Eq. *(4)*
$\bar{\eta}_s$	effectiveness factor in steady case, Eq. *(12)*
Θ	dimensionless temperature
$\bar{\Theta}$	mean dimensionless temperature
λ	effective thermal conductivity of catalyst
ϱ	catalyst density
τ	dimensionless time, Eq. *(4)*

Indices

i	for conditions at the outer catalyst surface
o	for the initial state
s	for the stationary solution

REFERENCES

1. Hlaváček V., Kubíček M., Marek M.: J. Catal. *15*, 17 (1969).
2. Hlaváček V., Kubíček M., Marek M.: J. Catal. *15*, 31 (1969).
3. Lee J. C. M., Luss D.: A.I.Ch.E. J. *16*, 627 (1970).
4. Hlaváček V., Kubíček M.: J. Catal. *22*, 364 (1971).
5. Mitschka P., Schneider P.: This Journal *37*, 196 (1972).
6. Mitschka P., Schneider P.: This Journal *35*, 1617 (1970).
7. Hlaváček V., Marek M., Kubíček M.: This Journal *35*, 2124 (1970).
8. Prater C. D.: Chem. Eng. Sci. *8*, 284 (1958).
9. Mitschka P., Schneider P.: This Journal *36*, 54 (1971).
10. Korn G. A., Korn M. T.: *Mathematical Handbook for Scientists and Engineers.* McGraw-Hill, New York 1968.
11. Hlaváček V., Hofmann H.: Chem. Eng. Sci. *25*, 1517 (1970).

Translated by K. Hlavatý.