Transient Heat and Mass Transfer in a Porous Catalyst III.

Reaction with Finite Values of Sherwood and Nusselt Number. Effect of Volume Contraction*

V. HLAVÁČEK AND M. KUBÍČEK

*Department of Chemical Engineering, Institute of Chemical Technology,
Technická Str. 1903, Prague 6, Czechoslovakia*

The effects of the ratio of the Sherwood and Nusselt numbers Sh/Nu, reaction order, n, and volume-change coefficient, σ, on the region of instability for catalytic exothermic reactions are examined. An appropriate combination of these parameters enlarges the domain of instabilities of steady states. However, for common physical systems the mutual interaction of temperature and concentration cannot be responsible for limit cycles observed for a single catalytic particle.

INTRODUCTION

In our previous communications (2, 11) dealing with transient heat and mass transfer in a porous catalyst the conditions leading to undamped oscillations have been examined. However, the value of the Lewis number is too high in order to verify this phenomenon in reacting systems. The analysis has been performed for the following conditions: single reaction of first order occurring without volume change and moreover both Sherwood and Nusselt numbers, describing the transport of mass and heat at the interface, are infinite. The later assumption takes into consideration the same values of both concentration and temperature in the bulk flow and at the surface as well.

Very recently, Wicke and Beusch (1) have observed undamped oscillations of temperature in a single isolated pellet, hanging on a thermoelement wire, for the oxidation of hydrogen by oxygen on Pt–alumina. The amplitude of oscillations in question has been approximately 150°C. It is obvious from the experimental arrangement that only the pellet may be responsible for this

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phenomenon, and, therefore, the transient behavior of a chemical reaction being accompanied by heat and mass transfer in a porous structure is reanalyzed. Finally, the maximum physically permissible parameters have been chosen in order to examine in detail the regions of instability. The effect of the Nusselt and Sherwood numbers, reaction order, as well as volume contraction on the stability region will be investigated.

NOTATION

n	reaction order
x	dimensionless space coordinate
x_1	collocation point
y	dimensionless concentration

Greek Letters

β	coefficient of temperature rise in porous particle
β_1	first root of transcendental Eq. (16)
γ	dimensionless activation energy
δ	modified Thiele parameter, $\delta = \phi^2 \gamma \beta$
θ	dimensionless temperature
ρ_1	first root of transcendental Eq. (15)
σ	coefficient of volume change
τ	dimensionless time
ϕ	Thiele parameter

Lw   Lewis number
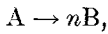Nu   Nusselt number
Sh   Sherwood number

Subscripts

s steady state
0   initial condition

Superscripts

*   critical value

TRANSPORT EQUATIONS

Let us assume a heterogeneous reaction,

$$A \rightarrow nB,$$

being accompanied by a volume change taking place in the porous structure of a catalyst. The mass and enthalpy balances, e.g., for the catalyst of the plate shape, may be written (2, 3).

$$\text{Lw} \frac{\partial y}{\partial \tau} = \frac{1}{1 + \sigma y} \frac{\partial^2 y}{\partial x^2} - \frac{\sigma}{(1 + \sigma y)^2} \left(\frac{\partial y}{\partial x} \right)^2$$
$$- \phi^2 y^n \exp \left(\frac{\theta}{1 + \theta/\gamma} \right), \quad (1)$$

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

subject to boundary conditions,

$$x = 1: y = 1 - \frac{1}{\text{Sh}} \frac{\partial y}{\partial x},$$
$$\theta = - \frac{1}{\text{Nu}} \frac{\partial \theta}{\partial x}, \quad (3)$$
$$x = 0: \frac{\partial y}{\partial x} = \frac{\partial \theta}{\partial x} = 0, \quad (4)$$

and initial conditions,

$$\tau = 0: y = y_0(x), \quad \theta = \theta_0(x). \quad (5)$$

It is obvious that for $\sigma = 0$, Eq. (1) corresponds to the common mass balance presented, for instance, in our former communication (2).

The equation describing transient mass transfer in a porous catalyst is highly nonlinear; moreover, the nonlinear source term contains the nonlinearities in coefficients and derivatives as well.

For a simplification of a set of nonlinear parabolic equations, collocation or linearization may be utilized (4). The linearization method can be used having the solution of a "linearized version" of the former nonlinear equation. For nonlinearities in coefficients and derivatives the collocation method is more convenient. After replacing the space derivatives in a given collocation point, we write, e.g., for a plate:

$$\frac{\partial^2 y}{\partial x^2} \Big|_{x = x_1} \approx 2.5 \left[y(1) - y \right];$$
$$\frac{\partial \theta^2}{\partial x^2} \Big|_{x = x_1} \approx 2.5 \left[\theta(1) - \theta \right] \quad (6)$$

$$\frac{\partial y}{\partial x} \Big|_{x = x_1} \approx 1.1180 \left[y(1) - y \right]. \quad (7)$$

The Jacobi polynomials are frequently recommended for diffusional problems (4, 10); therefore, the first node $x_1 = 0.4472$. For the infinite values of both Nusselt and Sherwood number Eqs. (6) and (7) may be rewritten:

$$\frac{\partial^2 y}{\partial x^2} \Big|_{x = x_1} \approx 2.5 \left(1 - y \right) \frac{\partial^2 \theta}{\partial x^2} \Big|_{x = x_1} \approx -2.5 \, \theta, \quad (8)$$

$$\frac{\partial y}{\partial x} \Big|_{x = x_1} \approx 1.1180 \left(1 - y \right). \quad (9)$$

After inserting Eqs. (8) and (9) in the set of Eqs. (1) and (2), a set of ordinary differential equations can be obtained:

$$\text{Lw} \frac{dy}{d\tau} = \frac{2.5}{1 + \sigma y} \left(1 - y \right)$$
$$- \frac{1.2499 \sigma}{(1 + \sigma y)^2} \left(1 - y \right)^2$$
$$- \phi^2 y^n \exp \left(\frac{\theta}{1 + \theta/\gamma} \right), \quad (10)$$

$$\frac{d\theta}{d\tau} = -2.5 \, \theta + \phi^2 \gamma \beta y^n \exp \left(\frac{\theta}{1 + \theta/\gamma} \right), \quad (11)$$

subject to initial conditions,

$$\tau = 0: y = y_0, \, \theta = \theta_0.$$

Eqs. (10) and (11) can be used for a study of effects of the coefficient σ on the stability of steady states.

For $\sigma = 0$, we can take use of the linearization principle (2, 4) and Eqs. (1) and (2) may be written

$$\text{Lw}\frac{dy}{d\tau} = \beta_1{}^2(1-y) - \phi^2 y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right), \tag{12}$$

$$\frac{d\theta}{d\tau} = -\rho_1{}^2\theta + \phi^2\gamma\beta y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right), \tag{13}$$

$$\theta = \frac{\beta_1{}^2}{\rho_1{}^2}\gamma\beta(1-y). \tag{19}$$

The effect of volume-change coefficient on stability, for nonsaddle steady states, can be studied from Eq. (20) (Sh = Nu → ∞, $n = 1$):

$$\text{Lw}^* = \frac{\dfrac{2.5(1+\sigma)}{(1+\sigma y)^2} - \dfrac{2.4998\sigma(1+\sigma)(1-y)}{(1+\sigma y)^3} + \phi^2\exp\left(\dfrac{\theta}{1+\theta/\gamma}\right)}{-2.5 + \dfrac{\phi^2\gamma\beta y}{(1+\theta/\gamma)^2}\exp\left(\dfrac{\theta}{1+\theta/\gamma}\right)}, \tag{20}$$

subject to initial conditions,

$$\tau = 0: y = y_0, \theta = \theta_0. \tag{14}$$

The coefficients ρ_1 and β_1 are the first positive roots of transcendental equations,

$$\text{tg}\rho = -\rho/\text{Nu}, \tag{15}$$

and

$$\text{tg}\beta = -\beta/\text{Sh}. \tag{16}$$

We can advantageously use Eqs. (12) and (13) for a study of effects of the reaction order and the ratio of Nusselt and Sherwood numbers on the stability of particular steady states.

ASYMPTOTIC STABILITY

For the sake of investigation of the asymptotic stability of Eqs. (10) and (11) as well as Eqs. (12) and (13), the first Ljapunov method can be used in the same manner as we have described in the first part of this series (2).

For instance, for $\sigma = 0$, the critical Lewis number Lw^* can be written:

$$\text{Lw}^* = \frac{\beta_1{}^2}{\rho_1{}^2} \cdot \frac{n - 1 - \dfrac{n}{y_s}}{1 - \theta_s/(1+\theta_s/\gamma)^2}, \tag{17}$$

where y_s and θ_s is the concentration and temperature, respectively. For the sake of brevity, the subscript s is further omitted. The steady state values y and θ may be calculated from Eqs. (18) and (19):

$$\beta_1{}^2(1-y) = \phi^2 y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right), \tag{18}$$

where the steady-state values y and θ may be determined from Eqs. (21) and (22):

$$2.5\theta = \phi^2\gamma\beta y^n \exp\left(\frac{\theta}{1+\theta/\gamma}\right), \tag{21}$$

$$\theta = \gamma\beta\left[\frac{1-y}{1+\sigma y} - 0.49997\left(\frac{1-y}{1+\sigma y}\right)^2\right]. \tag{22}$$

RESULTS AND DISCUSSION

(A) Agreement Between Model and Approximation

The value of Lw^* calculated from the two-dimensional model is shifted towards higher values of Lw. This observation is in agreement with our former computed results for first-order reaction and infinite Sherwood and Nusselt numbers (11). Referring to Figs. 1 and 2, the critical value of Lw^* is for the two-dimensional model Lw^*_ϵ (6,7), in turn, the approximation yields for the critical value of the Lewis number $\text{Lw}^* = 5.5$.

(B) Critical Lewis Number

(a) Effect of the ratio Sh/Nu. In our two former papers (5, 12) we have discussed the effect of the ratio Sh/Nu on the region of multiplicity. As a result, for in practice common ratios Sh/Nu, the region of multiplicity is shifted towards lower values of the parameter $\gamma\beta$, i.e., for an exothermic reaction which is not accompanied by an extreme heat evolution, multiple steady states may exist. According to the estimate of Carberry (6), the
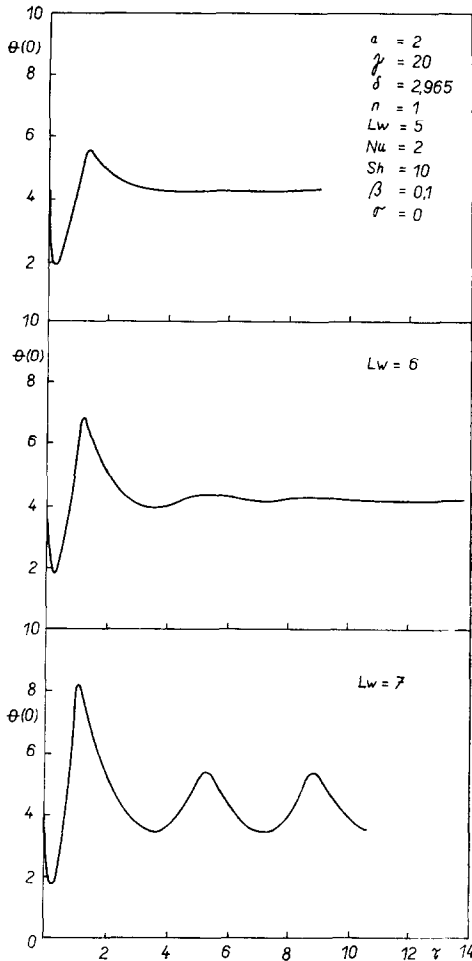
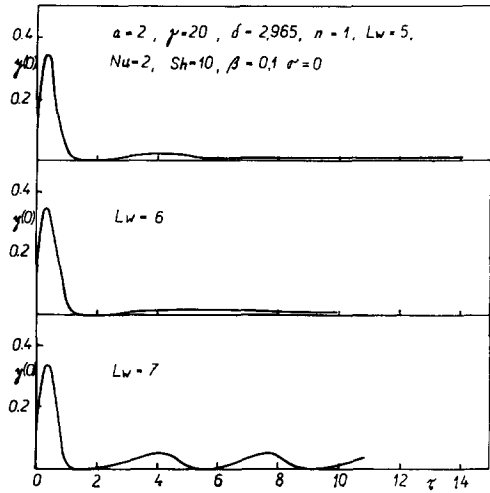FIG. 1. Time dependence of the temperature in the center of the particle. Two-dimensional model. Sphere.

FIG. 2. Time dependence of the concentration in the center of the particle. Two-dimensional model. Sphere.

dashed line. As long as $y < 0.34$, multiple solutions may not exist. For very high Sh/Nu ratios, the region of saddle points shifts almost to zero in concentration, i.e., the region of instability disappears again. It is obvious that an optimum Sh/Nu ratio exists where the critical Lewis number is a minimum. Referring to Figs. 4 and 5, the optimum Sh/Nu ratio ≈ 10

upper bound of the ratio Sh/Nu is approximately 10^4; however, for heterogeneous reactions this ratio may be in the region 100–600.

For a first-order reaction, the critical values (Lw^*) for the plate and sphere geometry are drawn in Figs. 1 and 2 as a function of the ratio Sh/Nu. For the values Sh/Nu > 1 the critical Lewis number Lw^* shifts towards lower values; however, multiple solutions always exist as we may observe in Fig. 3. For example, for Sh/Nu $= 10$ a saddle point exists in the region $y \, \epsilon \, \langle 0.34; \ 0.77 \rangle$ which is always unstable and, therefore, in this region the dependence $Lw^* = f(y)$ is drawn by a
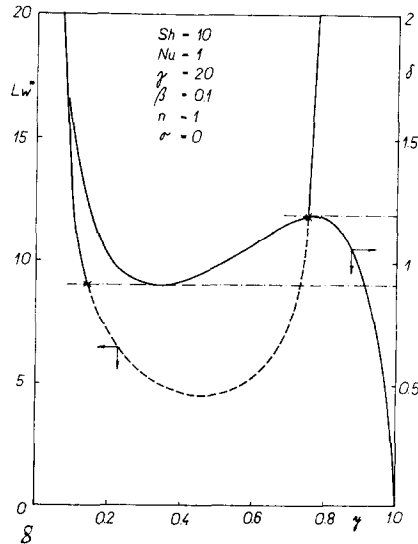

FIG. 3. Instability and multiplicity. Broken line indicates occurrence of the saddle points. Plate.
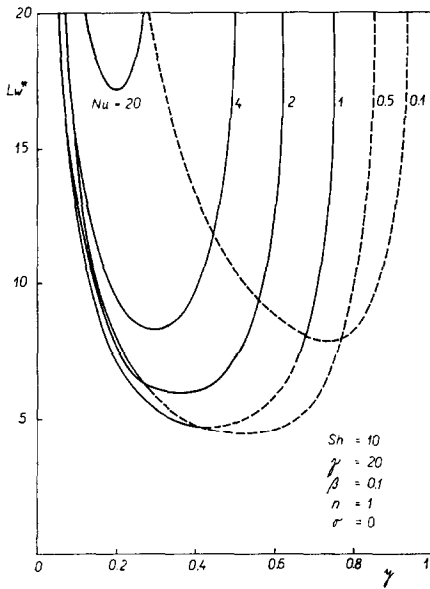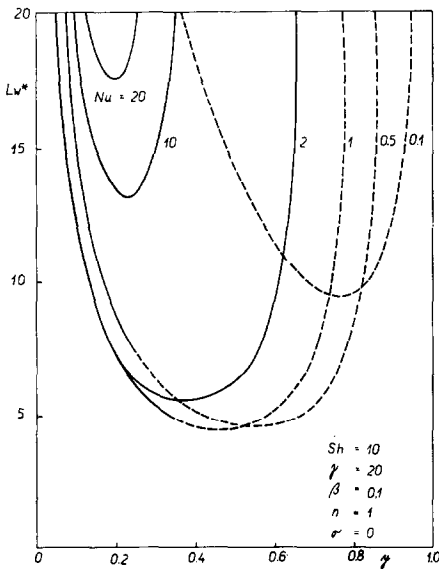
FIG. 4. Dependence of the critical Lewis number on the concentration in the particle. Plate. Broken line indicates occurrence of the saddle points.

which results in the minimum Lewis number $Lw^* \doteq 4.9$. For both $Sh \to \infty$ and $Nu \to \infty$ the minimum value $Lw^* \doteq 13.2$ may be estimated. Hence the optimum

ratio Sh/Nu suppresses essentially the critical Lewis number Lw^*; however, this value is far higher than can be expected in realistic physical systems.

Figures 4 and 5 are drawn for the same parameters for a plate and a sphere, respectively. After comparison of both dependences we can see a negligible effect of the geometry on the critical values of the Lewis number.

(b) **Effect of the reaction order.** The effect of the reaction order is indicated, for $Sh/Nu = 1$, in Fig. 6. The lower the reaction order, the smaller is the critical Lewis number. Therefore, a high reaction order suppresses the occurrence of both limit cycles and multiple solutions. As we have shown above the ratio $Sh/Nu > 1$ shifts the region of instability towards lower values of the critical Lewis number Lw^*. In turn, the higher reaction order decreases the domain of multiplicity. Hence we can expect a different optimum ratio of Sh/Nu. Referring to Fig. 7, the optimum ratio Sh/Nu can be extracted to be $Sh/Nu \approx 14$. However, the minimum value of the critical Lewis number Lw^*

FIG. 5. Dependence of the critical Lewis number on the concentration in the particle. Sphere. Broken line indicates the occurrence of the saddle points.
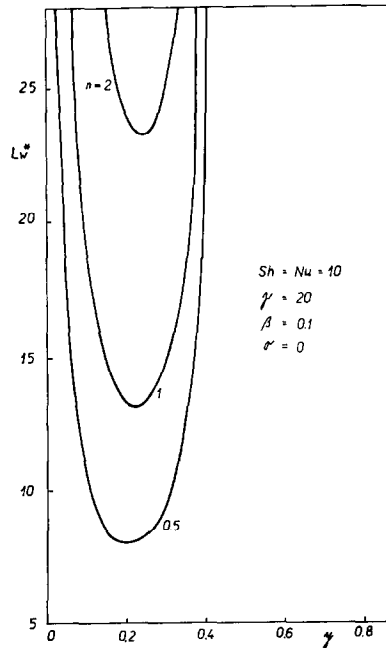

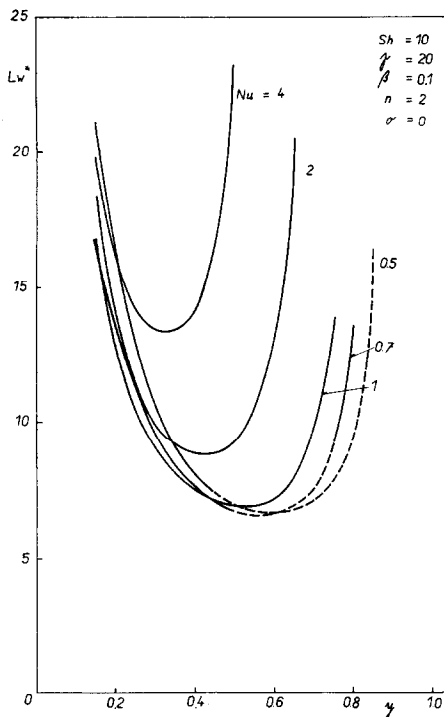FIG. 6. Dependence of the critical Lewis number on the reaction order. Plate.

FIG. 7. Dependence of the critical Lewis number on the concentration in the particle. Plate. Broken lines indicate occurrence of the saddle points.

FIG. 8. Dependence of the critical Lewis number on the concentration in the particle. Effect of the volume-change coefficient. Plate.

is slightly higher in comparison to the first order reaction.

(c) **Effect of the volume-change coefficient.** Recently Weekman (*3*) has shown that the volume contraction may result in an enlargement of the multiplicity region, i.e., the critical value $(\gamma\beta)^*$ can be expected to be lower. Now, let us study the influence of the volume-change coefficient on the stability of particular steady states. This dependence is depicted in Fig. 8 for parameters $\gamma = 40$ and $\beta = 0.05$. For reactions being accompanied by a volume contraction the critical Lewis number decreases in comparison to the case without volume change; in turn, for volume expansion a higher Lw^* results. For $\sigma = -0.75$, a minimum value $Lw^* \approx 1.9$ may be noted. However, this value seems to be too high in order to verify it in practice. Although the volume contraction may exhibit an essential effect on the magnitude of the $(\gamma\beta)^*$ as well as Lw^*, the influence can be supposed to be small because of
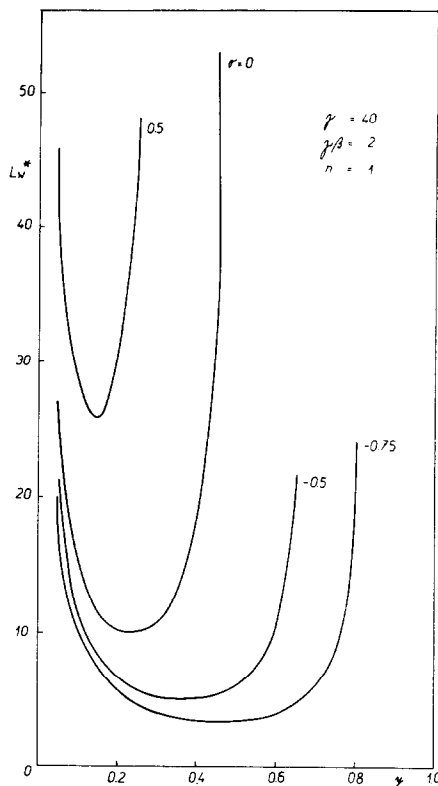
excess of one component, e.g., of hydrogen in hydrogenation reactions, which is common in carrying out exothermic heterogeneous reactions.

(*C*) *Maximum Transient Temperature in Catalyst Particle*

A number of authors, e.g., Wei (*8*), Luss (*9*), and others (*13*), have predicted excessive transient hot spots which can be substantially higher than the Prater temperature. In all these considerations or numerical studies, the magnitude of the Lewis number is very high. In Fig. 9, the trajectories are drawn for $Lw = 0.1$ which seems to be the upper bound for the overwhelming majority of exothermic catalytic reactions. This figure indicates that no transient hot spots exist and, therefore, one can expect that the Prater temperature is the upper bound for temperature also in transient cases. Horák (*7*) has ex-
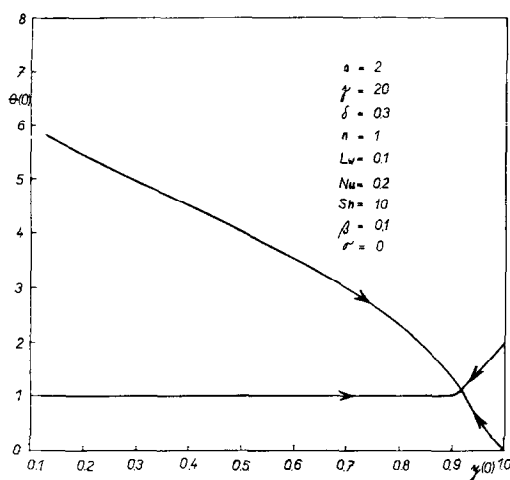
FIG. 9. Trajectories in the phase plane $\theta - y$. Sphere.

perimentally investigated the approach of the temperature to the steady state for the reaction $H_2 + O_2$ on a Pt catalyst. However, the transient hot spots have not been observed.

CONCLUSIONS

From the material presented, it is apparent that the occurrence of unstable steady states in a porous catalyst is not probable. Therefore, the simple interaction "decreasing concentration–increasing temperature" cannot be responsible for undamped oscillations which have been observed for a single particle. The effects of transport parameters on the interface, being formulated as a ratio of Sherwood and Nusselt numbers, as well as the influence of both reaction order and expan-

sion coefficient on the region of stability have been examined. This study has indicated that an appropriate combination of these parameters may lead to an essential enlargement of the instability region in comparison to the cases discussed in our former communications (2, 11).

We may expect that the observation of limit cycles by Wicke and Beusch (1) has to be caused by other physical effects. The authors of this communication believe that these oscillations are results, for instance, of autocatalytic kinetics. The analysis of such phenomena is now being performed.

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