Convective Stability in the Presence of a Catalytic Chemical Reaction

Part I. Stationary Instability

P. C. WANKAT and W. R. SCHOWALTER

Department of Chemical Engineering,
Princeton University, Princeton, New Jersey 08540

A linear analysis of hydrodynamic stability has been applied to a problem in which a fluid mixture is contained between two horizontal planes. One species diffuses to the lower plane where it is destroyed by a rapid exothermic or endothermic catalytic reaction. Results show that important coupling takes place between thermal and concentration fields. This coupling gives rise to unusual stabilizing or destabilizing effects, depending upon the value of Lewis number. Several examples are discussed. It is also shown how the results can be applied to other problems involving heat and mass transfer.

The importance of hydrodynamic stability to chemical engineering operations is a well recognized fact. Though perhaps the most familiar example is the effect of laminar-turbulent transition in pipe flow on transport of heat, mass, and momentum, other forms of instability are also pertinent. For example the effects which instabilities driven by buoyancy and interfacial forces have upon convective transport are well known (*1*, *2*). These instabilities can have a major influence on chemical engineering applications, such as liquid extraction, in which interphase transport is involved. It is known that interfacial instability can give rise to transport coefficients which are several times greater than values predicted from a model in which a stagnant interface is assumed (*3*). It is interesting that when combined heat and mass transfer occur, the stability of the system cannot, in general, be predicted from a simple superposition of the two single effects. Study of the equations for combined transport shows that the two processes are closely coupled to each other (*4*). In contrast to these rather thorough studies of physical processes, little attention has been given to the effect of chemical reaction on convective stability, although Ruckenstein and Berbente (*5*) have found that reactions in the bulk of a fluid can destabilize a convective system otherwise governed by changes in interfacial tension.

It is clear from the examples cited above and elsewhere that analysis of problems in hydrodynamic stability is possible only for rather simple geometries and restricted conditions. Consequently, the results of such analyses are not expected to provide predictions which can be utilized in a quantitative sense in systems of technological importance. For an engineer the power of stability analysis lies in its qualitative information. Idealized analyses can be very helpful in identifying the crucial variables for a given problem and the relative importance of the variables over a range of conditions. It is in this spirit that the present paper is offered.

We consider the effect of a catalytic reaction on convection induced by buoyancy. The system to be studied is a Newtonian fluid bounded by two infinite horizontal planes spaced a distance d apart. A reactant A diffuses from the top plane ($z = d$) through an inert fluid layer (component B) to the bottom plane ($z = 0$) where the reaction $A \rightarrow \text{Products}$ occurs. We make a number of simplifying assumptions about the system. These assumptions, although not essential to a solution, allow a reasonable balance between mathematical complexity and physical significance. The assumptions are: (1) The reaction is instantaneous. (2) The reaction is irreversible. (3) Products are passive (that is, the products have no effect upon either the catalyst or the fluid density).* Motion can be induced in the fluid by buoyancy forces caused by changes in density. The density is taken to be a function of concentration of reactant A and of temperature, but A is assumed to be sufficiently dilute so that (4) A is passive within the flow space, except for its effect upon fluid density. Temperature and concentration gradients are of course related through the heat of reaction.

We wish to find those conditions for which small disturbances to the one-dimensional profiles of concentration and temperature between the two planes neither grow nor decay in time. This method for dividing stable from unstable flows is the familiar procedure of classical linearized stability analysis which has been so successful for analysis of problems dealing with convective stability. Details of the method are readily available (*6*). We merely note that, in general, one must consider the marginal stability of both oscillatory and nonoscillatory states. In this paper conditions for nonoscillatory marginal stability, defined below, are considered for three different sets of boundary conditions at the top plane. In a companion paper (*7*) a modified Galerkin method is used to study the possibility of oscillatory stability.

P. C. Wankat is at the School of Chemical Engineering, Purdue University, Lafayette, Indiana 47907.

* In the Results and Discussion Section, we shall show how the results may be readily applied to certain other conditions.

BOUNDARY CONDITIONS AND STATIONARY STATE SOLUTION

Boundary conditions at $z = 0$ follow from the conditions stated earlier for reactant, reaction, and products. Thus we have

$$\mathbf{V} = \mathbf{0} \tag{1a}$$

$$C = 0 \tag{1b}$$

$$-\, l_R \mathcal{D} Q \frac{\partial C}{\partial z} = k \frac{\partial T}{\partial z} \tag{1c}$$

It is convenient to designate an exothermic or endothermic reaction by setting $l_R = +1$ or $l_R = -1$, respectively. We have assumed throughout that the wall at $z = 0$ is adiabatic, although any other stated value of heat transfer at the wall could also have been treated.

At the top plane $z = d$, we consider three possible sets of boundary conditions:

Case A: A rigid wall held at fixed temperature and concentration.

$$\mathbf{V} = \mathbf{0}; \quad C = C_d; \quad T = T_d \tag{2}$$

Case B: A rigid wall with fixed rates of heat and mass transfer.

$$\mathbf{V} = \mathbf{0}; \quad \partial C/\partial z = -\, l_C \beta_C; \quad \partial T/\partial z = -\, l_T \beta_T \tag{3}$$

Note that β_T and β_C are absolute values of the temperature and concentration gradients, respectively, with l_T and l_C being $\pm$ 1 as the temperature and/or concentration decrease or increase with z, respectively.

Case C: Fixed rates of heat and mass transfer across a flat stress-free surface, with negligible effects from interfacial tension.

$$\begin{gathered} W = \partial U/\partial z = \partial V/\partial z = 0 \\ \partial C/\partial z = -\, l_C \beta_C; \quad \partial T/\partial z = -\, l_T \beta_T \end{gathered} \tag{4}$$

To obtain a stationary solution to the transport equations, we add the usual restrictions: (5) Density is a linear function of temperature and of concentration of A. (6) The Boussinesq approximation is valid; that is, we need consider spatial variations of density only in the buoyancy term of the Navier-Stokes equation. In addition to standard descriptions of this assumption (6), validity of the Boussinesq approximation has been discussed in detail by Mihaljan (8). (7) The mass transfer rate is small so that its contribution to the bulk velocity is negligible.

The set of equations for which we require a time-independent solution is then

$$\begin{aligned} &\nabla \cdot \mathbf{V} = 0 \\ &\rho_0 \frac{D\mathbf{V}}{Dt} = -\, \nabla p + \mu \nabla^2 \mathbf{V} + \rho \mathbf{g} \\ &\rho_0 \hat{C}_p \frac{DT}{Dt} = k \nabla^2 T \\ &\frac{DC}{Dt} = \mathcal{D} \nabla^2 C \\ &\rho = \rho_0 [1 - \alpha_T (T - T_0) - s \alpha_C (C - C_0)] \end{aligned} \tag{5}$$

where $s = \pm$ 1 as $\partial \rho / \partial C \lessgtr 0$. A solution compatible with the boundary conditions is

$$\overline{\mathbf{V}} = \mathbf{0}; \quad \overline{C} = b_1 z + b_2; \quad \overline{T} = b_3 z + b_4 \tag{6}$$

where

Case A:

$$\begin{gathered} b_1 = C_d/d; \quad b_2 = 0 \\ b_3 = -\, (\mathcal{D}Q/kd) l_R C_d \\ b_4 = T_d + l_R \mathcal{D} Q C_d / k \end{gathered} \tag{7}$$

Cases B and C:

$$\begin{gathered} b_1 = -\, l_C \beta_C; \quad b_2 = 0 \\ b_3 = -\, l_T \beta_T = l_C l_R (\mathcal{D}Q/k) \beta_C \end{gathered} \tag{8}$$

The constant b_4 is not specified by the boundary conditions for cases B and C.

For the problem of major interest in this paper $l_C = -1$ since the concentration gradient is positive. Also, l_R must equal l_T because an exothermic reaction will produce a negative temperature gradient. Note that β_C and β_T are not independent. From Equations (7) and (8) we have, for all three cases

$$\beta_T = \frac{\mathcal{D}Q}{k} \beta_C \tag{9}$$

Although the stationary state solutions given by Equations (6) and either (7) or (8) are mathematically correct under all conditions, it is well known that they provide a correct physical description of the situation only at sufficiently low values of density gradient. Outside this range, heat and mass transfer are affected by convection and the purely conductive and diffusive solutions given above do not apply. In the next section we employ a linear stability analysis to determine those conditions under which heat and mass transfer will be accelerated by convective motion.

STABILITY ANALYSIS

Velocity, temperature, pressure, and concentration are all written in terms of the stationary state solution and an infinitesimal perturbation from this solution (6):

$$\mathbf{V} = \overline{\mathbf{V}} + \hat{\mathbf{v}}; \quad T = \overline{T} + \hat{\theta}; \quad p = \overline{p} + \hat{\delta p}; \quad C = \overline{C} + \hat{\xi} \tag{10}$$

Equations (10) are substituted into Equations (5) and the resulting equations are linearized by neglecting terms which are second order in the perturbations and in spatial derivatives of the perturbations. Upon subtraction of the stationary state solution, one obtains a set of differential equations for the perturbations which, when expressed in dimensionless form, are

$$\begin{gathered} \nabla \cdot \mathbf{v} = 0 \\ \frac{\partial \mathbf{v}}{\partial \tau} = -\, \nabla \delta p + \nabla^2 \mathbf{v} + R_T^{1/2}\, \theta \mathbf{k} + s R_C^{1/2}\, \xi \mathbf{k} \\ N_{Pr} \frac{\partial \theta}{\partial \tau} = l_T R_T^{1/2} w + \nabla^2 \theta \\ N_{Sc} \frac{\partial \xi}{\partial \tau} = l_C R_C^{1/2} w + \nabla^2 \xi \end{gathered} \tag{11}$$

To be compatible with the boundary conditions stated earlier, we must set

$$\mathbf{v} = \mathbf{0}; \quad \xi = 0; \quad l_R N_H \frac{\partial \xi}{\partial z} = -\, \frac{\partial \theta}{\partial z} \text{ at } z = 0 \tag{12}$$

while at $z = 1$ we have

Case A:

$$\mathbf{v} = \mathbf{0}; \quad \xi = \theta = 0 \tag{13a}$$

Case B:

$$\mathrm{v} = 0; \quad \frac{\partial \xi}{\partial z} = \frac{\partial \theta}{\partial z} = 0 \tag{13b}$$

Case C:

$$w = \frac{\partial u}{\partial z} = \frac{\partial v}{\partial z} = \frac{\partial \xi}{\partial z} = \frac{\partial \theta}{\partial z} = 0 \tag{13c}$$

Following standard methods (*6*), we consider one set of Fourier components for the disturbances:

$$\begin{aligned} \mathrm{v} &= \mathrm{v}(z) \exp[i(a_x x + a_y y) + \sigma\tau] \\ \theta &= \theta(z) \exp[i(a_x x + a_y y) + \sigma\tau] \\ \xi &= \xi(z) \exp[i(a_x x + a_y y) + \sigma\tau] \\ \delta p &= \delta p(z \exp[i(a_x x + a_y y) + \sigma\tau] \end{aligned} \tag{14}$$

In general σ is complex so we write $\sigma = \sigma_r + i\sigma_i$. When $\sigma_r < 0$ the perturbations decay and the system is stable to infinitesimal perturbations. When $\sigma_r > 0$ the perturbations grow and the system is unstable. One seeks the divisions between these two conditions by setting $\sigma_r = 0$ and locating conditions for neutral stability. As mentioned earlier, we restrict the analysis here to cases where the principle of exchange of stabilities is valid, that is, to cases where $\sigma_i = 0$ whenever $\sigma_r = 0$. This is called stationary, or direct, instability. We defer treatment of oscillatory instability ($\sigma_r = 0$, $\sigma_i \neq 0$) to another paper (*7*).

After Equations (14) are substituted into Equations (11) to (13), u, v, w, θ, and δp are eliminated. Since we are interested in conditions for neutral stationary instability, we may set $\sigma = 0$. We obtain the result that at conditions of marginal stability, the following eighth-order ordinary differential equation is obeyed:

$$a^2(A1)(D^2 - a^2)\,\xi = -\,(D^2 - a^2)^4 \xi \tag{15}$$

where $A1 = l_T R_T + s l_C R_C$ and ξ now refers to $\xi(z)$.

$$a^2 = a_x^2 + a_y^2$$

$$D = \frac{d}{dz}$$

Boundary conditions at $z = 0$ are

$$\begin{aligned} (D^2 - a^2)\xi &= D(D^2 - a^2)\xi = \xi = 0 \\ (A2)a^2 D\xi &= D(D^2 - a^2)^3 \xi \end{aligned} \tag{16}$$

where $A2 = l_C[l_R R_C^{1/2}\, R_T^{1/2} N_H - s R_C]$. The boundary conditions at $z = 1$ are

Case A:

$$(D^2 - a^2)\xi = D(D^2 - a^2)\xi = (D^2 - a^2)^3\, \xi = \xi = 0 \tag{17a}$$

Case B:

$$(D^2 - a^2)\xi = D(D^2 - a^2)\xi = D(D^2 - a^2)^3\, \xi = D\xi = 0 \tag{17b}$$

Case C:

$$(D^2 - a^2)\xi = D^2(D^2 - a^2)\xi = D(D^2 - a^2)^3\, \xi = D\xi = 0 \tag{17c}$$

The general solution to Equation (15) is easily obtained for conditions $A1 \geqq 0$, $\tau \geqq 1$ (*6*, *9*).

$$\begin{aligned} \xi = {} & B_1 \cosh az + B_2 \sinh az + B_3 \cos q_0 z + B_4 \cosh qz \\ & + B_4^* \cosh q^* z + B_5 \sin q_0 z + B_6 \sinh qz + B_6^* \sinh q^* z \end{aligned} \tag{18}$$

where the B_i are complex constants and

$$q_0 = a(\tau - 1)^{1/2} \qquad q = q_1 + iq_2$$

$$q^* = q_1 - iq_2 \qquad \tau = \left(\frac{(A1)}{a^4}\right)^{1/3}$$

$$\begin{aligned} q_1 &= a\left\{\frac{1}{2}(1 + \tau + \tau^2)^{1/2} + \frac{1}{2}\left(1 + \frac{1}{2}\tau\right)\right\}^{1/2} \\ q_2 &= a\left\{\frac{1}{2}(1 + \tau + \tau^2)^{1/2} - \frac{1}{2}\left(1 + \frac{1}{2}\tau\right)\right\}^{1/2} \end{aligned} \tag{19}$$

The B_i are determined by the eight boundary conditions. Constants B_1, B_2, B_3, and B_5 were found in terms of B_4, B_4^*, B_6, and B_6^* using the boundary conditions at $z = 0$. Then, from the boundary conditions at $z = 1$, four homogeneous linear equations in B_4, B_4^*, B_6, and B_6^* are obtained. The condition that these constants be independent requires that the determinant of the coefficient matrix vanish. This requirement then provides the conditions for neutral stability.

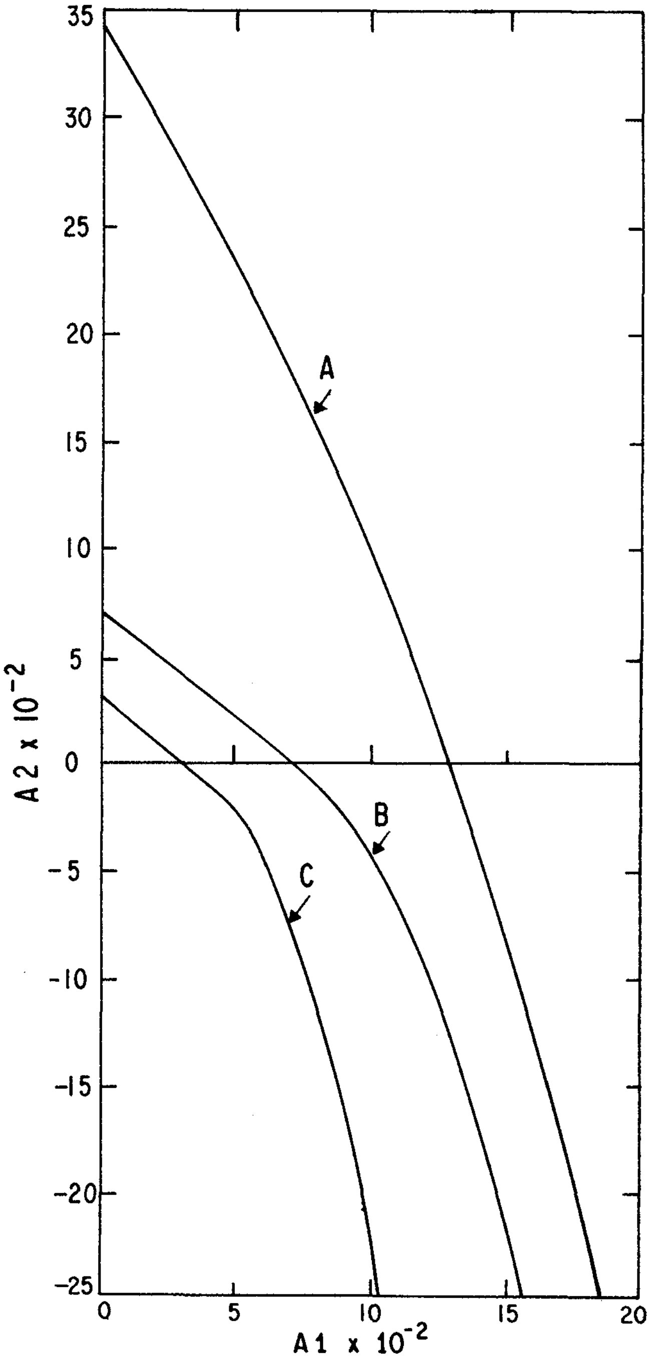

Fig. 1. Neutral stability curves for boundary conditions *A*, *B*, and *C*.

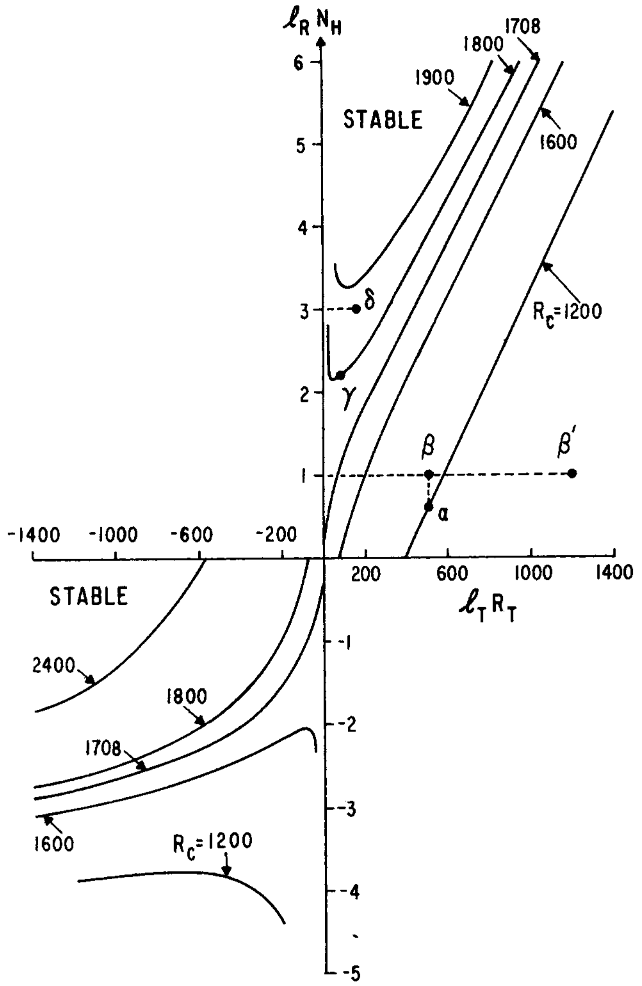

Fig. 2. Neutral stability curves for case A.

RESULTS AND DISCUSSION

We immediately see from Equations (15) to (17) that the parameters which determine stability characteristics can be combined into two variables, $A1$ and $A2$, along with a wave number a. Critical conditions are found by choosing successive values of $A1$ and, for each value of $A1$, determining the lowest numerical value of $A2$ with which Equations (15) to (17) can be solved. The value of a at which the lowest value of $A2$ is obtained is then the critical wave number. The critical value of a is not of primary concern to us here, although it has been calculated and is available (9).

Catalytic Reaction

The most efficient way of presenting the results is simply to plot the neutral curve which relates $A2$ to $A1$ at conditions of marginal stability. The resulting envelopes are shown in Figure 1 for boundary conditions A, B, C. Stable and unstable regions are to the left and right, respectively, of each envelope. It is interesting to note that the system becomes increasingly less stable as boundary conditions are changed from case A to B to C. This trend can be explained by the successive relaxation of constraints on the magnitude of the perturbations at $z = d$. (Recall that, according to assumptions employed in the analysis, spatial derivatives of the perturbations cannot exceed the order of magnitude of the perturbations themselves.) In case A all of the perturbations must be zero at $z = d$. For case B the velocity perturbations are constrained at $z = d$, but temperature and concentration are not. For case C only the z component of the velocity perturbation is constrained.

Although all essential information is available in Figure 1, the subtle interplay between dimensionless groups, and the relation of this problem to simpler limiting cases, can be made evident from other representations of the results. We limit the subsequent discussion to results for case A, although cases B and C have been handled similarly (9).

It would seem natural to plot stability curves on a space made up of two of the relevant dimensionless groups with the third as a parameter. This has been done in Figure 2. Since l_R and l_T have the same sign, no curves are shown in the second and fourth quadrants. The curve for $R_C = 1{,}708$ (1707.765...) is of fundamental significance. It is seen from Figure 2 that this curve passes through the origin and divides single- from double-valued neutral curves for constant R_C. If $N_H = 0$ any value of $R_C > 1{,}708$ must represent an unstable condition for $l_T R_T \geqq 0$. This critical value corresponds to the results which are known for mass transfer with boundary conditions of case A but with no chemical reaction (4).

In discussing the physical meaning of Figure 2, we concentrate on points in the first quadrant. Consider a system with $R_C = 1{,}200$, which is at a marginally stable condition, as shown by α in Figure 2. Clearly, any change which at constant R_C shifts R_T to the right of the envelope for $R_C = 1{,}200$, will produce an unstable condition. We call such changes destabilizing. Conversely, we also refer to changes in conditions which are stabilizing. In this regard it is interesting to note the effect of increasing N_H (that is, increasing the exothermic heat of reaction) but holding other parameters constant. This is shown by the change from α to β in Figure 2. We note the unexpected result that this

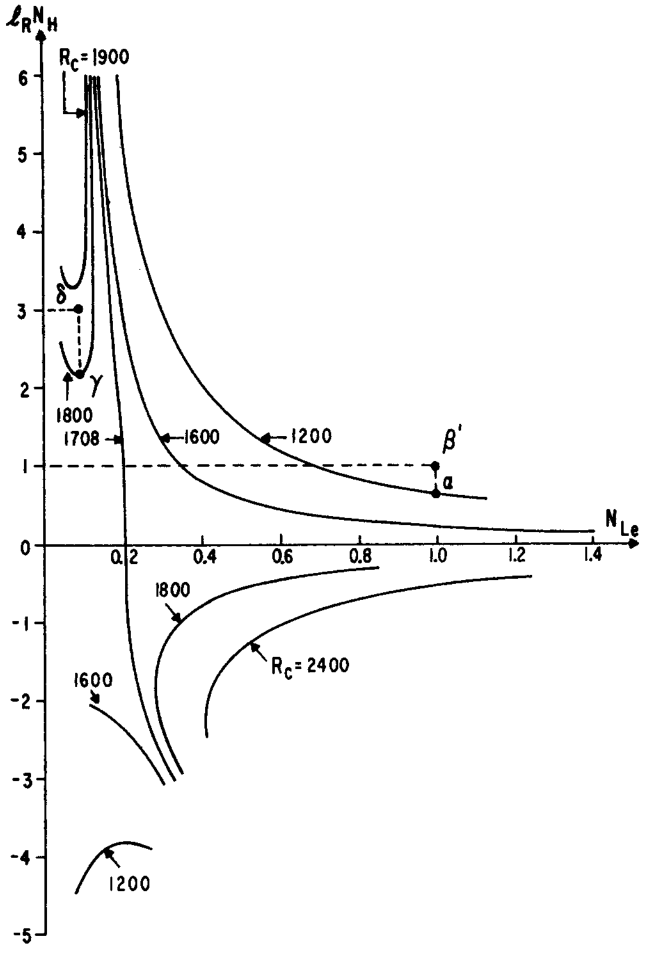

Fig. 3. Neutral stability curves for case A. Effect of Lewis number.

is a stabilizing change. To account for this apparent anomaly, one must recognize that for a given fluid, the three parameters shown in Figure 2 are not independent. We see from Equation (9) that the gradients in temperature and concentration are coupled. Hence we obtain

$$R_T = R_C\, N_{Le}^2\, N_H^2 \tag{20}$$

where the Lewis number, $N_{Le} = N_{Pr}/N_{Sc} = \mathcal{D}/\kappa$, is a ratio of the ease of molecular transport of mass relative to that of heat. Equation (20) is suggestive of a third means of presentation of results. Since for any given fluid we have $N_{Le} =$ const., the results have been plotted in Figure 3 with N_H, N_{Le}, and R_C as the pertinent variables. We can now see how the value of Lewis number governs whether an increasing heat of reaction will be stabilizing or destabilizing.

Suppose we consider a gas (for gases $N_{Le} \cong 1$) with $N_{Le} = 1$ and $R_C = 1{,}200$ at the condition of marginal stability α, discussed earlier, and now shown in Figure 3. We have $N_H = 0.65$. Now suppose that the heat of reaction is altered to, say, $N_H = 1.00$. One finds that the state is now represented by β'. Since R_C is still 1,200 the system has become destabilized, as is evident from the position of β', which has also been plotted in Figure 2. Thus we see that the transition $\alpha \rightarrow \beta$, mentioned earlier, is not compatible with a constant value of N_{Le}.

Although one would expect greater heat liberation at the bottom plate to be a destabilizing influence, such is not always the case. Let us consider for a second example a liquid, which would typically have a Lewis number of 0.01 to 0.1. The point γ in Figures 2 and 3 corresponds to a fluid with $N_{Le} = 0.1$ at the condition of marginal stability for $R_C = 1{,}800$ and $N_H = 2.15$. Then, by Equation (20) $R_T = 83.2$. Now suppose the reaction changes to $N_H = 3.0$. The new state is shown by δ in Figures 2 and 3, and we see that the system has been stabilized. In this case the increase in R_T which, as is seen from Equation (20), must accompany an increase in N_H is small as a consequence of the small value of N_{Le}. Thus the increase in R_T is less than the increase in $(R_T)_{\text{crit.}}$ which occurs as one moves along the stability envelope for $R_C = 1{,}800$, shown in Figure 2. [When $R_C = 1{,}800$ and $N_H = 3.0$, $(R_T)_{\text{crit.}} \cong 305$.] This change in the effect of coupling between heat and mass transfer is the result of a change which occurs in the relative importance of two competing effects as one alters the Lewis number. Buoyancy forces caused by increases in temperature which arise from an exothermic reaction ($l_R = +1$) are of course destabilizing. However, it is apparent from Equation (12) that at $z = 0$ $\partial\xi/\partial z$ and $\partial\theta/\partial z$ must have opposite signs. Thus if in the region near $z = 0$ $\partial\theta/\partial z < 0$, then $\partial\xi/\partial z > 0$ and vice-versa. Hence a destabilizing effect due to temperature perturbations will be offset, through the boundary conditions, by a stabilizing effect (assuming $s = +1$) due to concentration perturbations.

Alternate Interpretations

Combined Heat and Mass Transfer with No Reaction. With only a slight alteration the results obtained above can be used to interpret the case where heat and mass transfer occur but are not coupled through a chemical reaction. In this case Equation (1*c*) is no longer applicable. Now the appropriate boundary conditions at $z = 0$ for the stationary state solution are Equations (1*a*), (1*b*), and

$$\frac{\partial T}{\partial z} = -\, l_T \beta_T \tag{21}$$

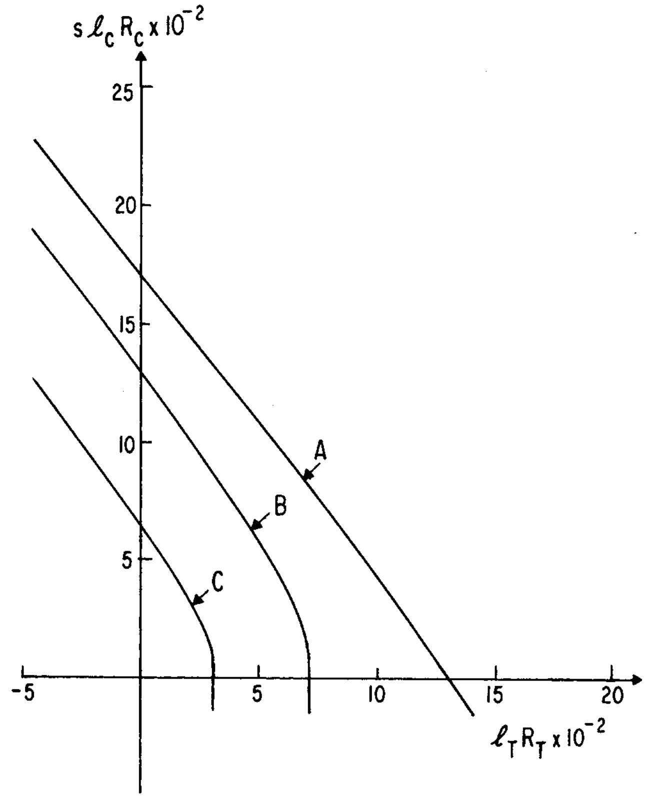

Fig. 4. Neutral stability curves for combined heat and mass transfer with no reaction. Cases A, B, and C.

Conditions at $z = 1$ are the same as those employed earlier for cases A, B and C. Since Equation (21) is not a limiting case of Equation (1*c*) the stationary state solution is altered. However, the form of the differential equations governing the perturbations is not changed, since from Equation (21) we still have

$$\frac{\partial\theta}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{22}$$

Thus we may use the analysis developed above except that we now have

$$\begin{aligned} A1 &= l_T R_T + s l_C R_C \\ A2 &= -\, s l_C R_C \end{aligned} \tag{23}$$

Neutral stability curves are shown for cases A, B, and C in Figure 4, which is readily obtained from Figure 1. Case A exhibits the expected behavior; i.e., as $sl_C R_C$ decreases, the critical value of $l_T R_T$, increases. However, for cases B and C one notes that negative values of $sl_C R_C$ do not cause further stabilization. This is due to the fact that for $sl_C R_C \leqq 0$ the critical wave number for cases B and C is zero, the problem becomes degenerate, and there is no coupling between heat and mass transfer. Qualitative similarity exists between our results and those of Nield (*4*), who analyzed the coupling of heat and mass transfer for boundary conditions different from those given here.

Reaction A → m P *with Diffusion of Products but No Heat of Reaction.* The results presented here can also be modified to apply to the situation where a reaction is occurring with negligible heat of reaction. However, we shall now suppose that the density of the fluid is affected by both the concentration C_A of reactant and C_P of products. As before, we must assume that A and P are present in small quantities in an inert carrier B. At steady state we have equal and opposite mass fluxes of A and P through stagnant B so that a boundary condition at $z = 0$ is

$$l_Q \mathcal{D}_{AB} \beta_A = -\, \mathcal{D}_{PB} \beta_P \tag{24}$$

where β_P is the absolute value of concentration gradient of product. It is of course assumed that A and P are passive to each other with respect to mass transfer. l_Q is $+1$ if a reaction occurs. By setting $l_Q = 0$ one may apply these results to the case where two components, A and P, of a mixture are diffusing independently of each other. For the conditions stated one merely reinterprets the heat transfer terms used earlier as analogous mass transfer effects. Thus for the stationary solution we apply Equation (6), replacing $\overline{T}$ by $\overline{C}_P$ and $\overline{C}$ by $\overline{C}_A$. Changes in arbitrary constants of Equation (6) are

Case A:

$$b_3 = -(\mathcal{D}_{AB}/\mathcal{D}_{PB})\,\frac{C_A(z=d)}{d}$$

$$b_4 = C_P(z=d) + (\mathcal{D}_{AB}/\mathcal{D}_{PB})C_A(z=d)$$

Cases B and C:

$$b_1 = -l_A\beta_A;\; b_2 = 0;\; b_3 = -l_P\beta_P = (\mathcal{D}_{AB}/\mathcal{D}_{PB})l_Al_P\beta_A$$

In the analysis presented earlier, θ now becomes a perturbation in concentration of P and ξ becomes the perturbation in concentration of A. Equations (15), (16), and (17) are obtained, with the exception that

$$\begin{aligned} A1 &= s_Pl_PR_P + s_Al_AR_A \\ A2 &= l_A\{[R_PR_A(\alpha_P/\alpha_A)]^{1/2}s_Pl_Q - s_AR_A\} \end{aligned} \tag{25}$$

Interpretation of the figures is then straightforward.

SUMMARY

We have indicated how hydrodynamic convective stability can be influenced by the coupling which occurs between heat and mass transfer when a catalytic reaction takes place with accompanying liberation or absorption of heat. The problem treated is the idealized one of an instantaneous irreversible reaction occurring at the lower of two parallel infinite horizontal planes which bound the fluid. However, the results should have qualitative significance for less idealized situations. It is found that the heat of reaction can be a stabilizing or destabilizing influence, depending upon the value of the Lewis number. Two alternate interpretations of the results are also discussed briefly: the case where no reaction occurs; and the case where the heat of reaction is negligible, but where buoyancy is affected by concentration of products. The analysis corresponds, in limiting cases, to known results of earlier work. Although the analysis presented here is limited to nonoscillatory or direct instability, it is unlikely that oscillatory instability is of major importance (7).

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NOTATION

$A1$ = $l_TR_T + sl_CR_C$, or as defined by Equation (25)
$A2$ = $l_C[l_RN_H(R_CR_T)^{1/2} - sR_C]$, or as defined by Equation (23) or (25)
a = $(a_x^2 + a_y^2)^{1/2}$
a_x = wave number as defined by Equation (14)
a_y = wave number as defined by Equation (14)
C = concentration, mass/volume
$\hat{C}_p$ = heat capacity per unit mass
D = d/dz
$\mathcal{D}$ = mass diffusivity
d = distance between horizontal bounding planes
g = acceleration due to gravity
k = thermal conductivity
l_A, l_P = ± 1 as the concentration of A (l_A) or P (l_P) decreases or increases with z, respectively, for the alternate interpretation $A \rightarrow m\,P$ with no heat of reaction but with diffusion of products
l_C = ± 1 as the concentration of A decreases or increases, respectively, with z
l_R = ± 1 for an exothermic or endothermic reaction, respectively
l_T = ± 1 as the temperature decreases or increases, respectively, with z
N_H = $\dfrac{Q\alpha_T}{\alpha_C\,\rho_0\,\hat{C}_p}$
N_{Le} = $\mathcal{D}/\kappa$
N_{Pr} = ν/κ
N_{Sc} = $\nu/\mathcal{D}$
p = pressure
Q = heat of reaction per unit mass of reactant
R_A = $\dfrac{\alpha_A\beta_Agd^4}{\nu\mathcal{D}_{AB}}$ [Equation (25)]
R_C = $\dfrac{\alpha_C\beta_Cgd^4}{\nu\mathcal{D}}$
R_P = $\dfrac{\alpha_P\beta_Pgd^4}{\nu\mathcal{D}_{PB}}$ [Equation (25)]
R_T = $\dfrac{\alpha_T\beta_Tgd^4}{\kappa\nu}$
s = ± 1 as the density of the system decreases or increases, respectively, with increasing concentration C
T = temperature
t = time
U, V, W = x, y, and z components, respectively, of velocity
u, v, w = x, y, and z components, respectively, of velocity perturbation
$\mathbf{V}$ = velocity
$\mathbf{v}$ = velocity perturbation
x, y = rectangular Cartesian coordinates in a horizontal plane
z = vertical coordinate, dimensional or dimensionless

Greek Letters

α_A = $|\partial \ln\rho/\partial C_A|$ [Equation (25)]
α_C = $|\partial \ln\rho/\partial C|$
α_P = $|\partial \ln\rho/\partial C_P|$ [Equation (25)]
α_T = $|\partial \ln\rho/\partial T|$
β_A = $|d\overline{C}_A/dz|$ [Equation (24)]
β_C = $|d\overline{C}/dz|$
β_P = $|d\overline{C}_P/dz|$
β_T = $|d\overline{T}/dz|$
δp = pressure perturbation
θ = temperature perturbation
κ = thermal diffusivity = $k/(\rho_0\,\hat{C}_p)$
μ = viscosity
ν = kinematic viscosity = μ/ρ_0
ξ = concentration perturbation = $\xi(x, y, z, \tau)$ or = $\xi(z)$ [Equation (14)]

ρ = density
σ = growth rate for disturbance [Equation (14)]
σ_r, σ_i = real and imaginary parts, respectively, of growth rate
τ = $t\nu/d^2$ or, in Equation (19), = $(Al/a^4)^{1/3}$

Superscripts

$\bar{\ }$ = stationary state solution
$\hat{\ }$ = dimensional quantity

Subscripts

A = reactant A for the reaction $A \rightarrow m\,P$ with diffusion of products but no heat of reaction
d = evaluated at $z = d$ $(z = 1)$
P = product P for the reaction $A \rightarrow m\,P$ with diffusion of P but no heat of reaction
0 = evaluated at $z = 0$

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Application of Empirical Rate Expressions and Conservation Equations to Photoreactor Design

FRANCIS P. RAGONESE and JOHN A. WILLIAMS

Department of Chemical Engineering,
Northeastern University, Boston, Massachusetts 02115

An empirical rate expression was obtained for the photolysis of tetrachloroplatinic acid (TCPA). The data used to evaluate the parameters of the rate expression were obtained in an elliptical photoreactor operated at high recycle rates in order to maintain a uniform reactant concentration within the photoreactor. A low-pressure mercury lamp provided light at a wavelength of 2,537Å. The light was assumed to enter the reactor radially and uniformly with respect to both the axial and angular directions.

This rate expression was incorporated in a reactant conservation equation which was solved to obtain the predicted conversion of TCPA in an elliptical photoreactor operating in the laminar regime. Solutions of the conservation equation were obtained for photoreactors of two different diameters and for three different lengths.

Experimentally observed conversions of TCPA in the laminar regime agreed well with the theoretical solutions except at conversions above 55%, where a solid precipitate apparently caused the lack of agreement.

The rational design and scale-up of photoreactors has been a subject of increasing interest to chemical engineers in recent years. The literature in this field has been critically reviewed by Cassano, Silveston, and Smith (5). The specific problem of photoreactor scale-up has been considered by Harris and Dranoff (9), who presented experimental results relating to the radial scale-up of an annular photoreactor, and by Dolan, Dimon, and Dranoff (7), who reported on the results of a dimensional analysis of an elliptical reflector-tubular photoreactor system. The tetrachloroplatinic acid photolysis reaction was utilized in both studies.

The scale-up methods developed by these authors do not require an explicit reaction rate expression. The method of Harris and Dranoff (9) is restricted to radial scale-up of annular photoreactors whose contents are well mixed.

The method of dimensional analysis was used by Dolan, Dimon, and Dranoff (7) to correlate conversion data obtained in a tubular flow photoreactor for a range of flow rates and length-to-diameter ratios. Since the correlation utilizes optical density as a parameter, this method cannot be used to predict photoreactor performance under conditions of varying optical density unless experimental data are available for every optical density encountered in the scale-up problem.

The purpose of the present work is to demonstrate an alternate approach to the problem of photoreactor scale-up. In this approach an empirical reaction rate expression, reactant continuity equation, and radiation equation are applied to the problem of predicting the performance of

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F. P. Ragonese is with Shell Chemical Company, Woodbury, New Jersey 08096. Correspondence concerning this article should be addressed to J. A. Williams.