h = heat transfer coefficient
h_{KA}, h_{KB} = heat of adsorption for A and B, dimensionless
K_A, K_B = dimensionless adsorption equilibrium constant for A and B
k_0 = main reaction rate constant
k_{f1}, k_{f2} = fouling reaction rate constant for parallel and series fouling, respectively
km = mass transfer coefficient
Nu^* = modified Nusselt number, $Rh/\kappa e$
R = radius of pellet
S = activity
Sh^* = modified Sherwood number, $R\, k_m/De_A$
t = process time

Greek Letters

α = geometric factor
β = thermicity factor
$\gamma, \gamma_{f1}, \gamma_{f2}$ = dimensionless activation energy parameter for the main, parallel fouling and series fouling reaction
δ = dimensionless particle radial coordinate
η = effectiveness factor
η_0 = effectiveness factor at $\tau = 0$
κe = effective conductivity of particle
τ = dimensionless time
ϕ = Thiele modulus
θ = dimensionless particle temperature
θ_s = dimensionless particle surface temperature

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A Note on the Upper and Lower Solutions of a Mass Transfer Problem with Chemical Kinetics

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There has recently been great interest in applying the Nagumo Lemma (Walter, 1970) to construct upper and lower solutions to practical physical problems (Tam, 1976; McDaniel and Murthy, 1976, 1977). It has already been pointed out by Tam and Ng (1977) that the Nagumo Lemma can be employed to construct upper and lower solutions to problems which can be described by a nonlinear, parabolic, partial-differential equation. The object of this note is to expand the family of problems to which the Nagumo Lemma can be successfully applied to give upper and lower solutions to problems in chemical engineering.

In this note we construct upper and lower solutions to a system of weakly coupled parabolic equations arising from the study of a mass transfer problem with chemical kinetics (Brian et al., 1961). The problem to be considered is that in which a gaseous species A dissolves into the liquid phase and then reacts irreversibly with species B according to a second-order chemical reaction equation. Species B is a nonvolatile solute which has been dissolved into the liquid phase prior to its introduction into the gas absorber. It is assumed that the gas phase resistance to absorption is negligible, and thus the concentration of species A at the gas-liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase.

The governing equations of this physical phenomenon can be expressed in terms of the following dimensionless variables (Brian et al., 1961):

$$\frac{\partial \alpha}{\partial \theta} = \frac{\partial^2 \alpha}{\partial \xi^2} - \Gamma \alpha \beta \quad (1)$$

$$\frac{\partial \beta}{\partial \theta} = \Delta \frac{\partial^2 \beta}{\partial \xi^2} - \alpha \beta \quad (2)$$

subject to

$$\alpha(\xi, 0) = 0, \quad \alpha(0, \theta) = 1, \quad \alpha(\infty, \theta) = 0 \quad (3)$$

$$\beta(\xi, 0) = 1, \quad \frac{\partial \beta}{\partial \xi}(0, \theta) = 0, \quad \beta(\infty, \theta) = 1 \quad (4)$$

The asymptotic solutions of the above systems of equations have been obtained by Pearson (1963), where he examined the following cases.

1. The case for sufficiently small Γ, where there is little α concentration and the reaction is essentially absent. The solution is given by

$$\alpha = \text{erfc}\left(\frac{\xi}{2\sqrt{\theta}}\right) \tag{5}$$

2. The case where the proportional depletion of B due to the inward diffusion of A is negligible in the early stages. This occurs because of an initially high concentration of $B(\Gamma >> 1)$. Pearson calls this case the first-order reaction case. He shows that the solution is given by

$$\alpha = \frac{1}{2}\left\{ e^{-\xi\sqrt{\Gamma}}\text{erfc}\left(\frac{\xi}{2\sqrt{\theta}} - \sqrt{\Gamma}\theta\right) + e^{\xi\sqrt{\Gamma}}\text{erfc}\left(\frac{\xi}{2\sqrt{\theta}} + \sqrt{\Gamma}\theta\right)\right\} \tag{6}$$

In this note we shall construct the upper and lower solutions of α and β, valid for $\Gamma >> 0$, and show that when Γ is very small, the upper solution of α is identical to (5). When Γ is very large, the lower solution of α is exactly the same as (6). Thus, we recover Pearson's asymptotic solutions for extreme cases of Γ. Furthermore, since our upper and lower solutions are valid for all values $\Gamma \geqq 0$, this demonstrates that our constructed bounds offer an advantage over Pearson's asymptotic solution, as we shall see in the following.

CONSTRUCTION OF UPPER AND LOWER SOLUTIONS

Since it is the intent of this paper to construct upper and lower solutions, we shall assume that the system (1) to (4) has a unique solution. In essence, the Nagumo Lemma is applied to each of the given Equations (1) and (2), respectively, to establish single bounds and also serves to relate these bounds to each other. This technique will become more explicit in the formulations to follow. Firstly, we define the domain and boundaries of (1) and (2) as

$$G_p = \{(\theta, \xi) | 0 < \theta < T, 0 < \xi < \infty\} \quad \text{for some large } T$$

$$R_p = \{(\theta, \xi) | \theta = 0, 0 < \xi < \infty\} \; U\{(\theta, \xi) | \xi = 0, 0 < \theta < T\}$$

$$R_n = \{(\theta, \xi) | \xi = 0, 0 < \theta < T\}$$

Systems (1) to (4) have discontinuous initial and boundary conditions as well as conditions at infinity. In order to handle such systems, the following definition is made in order to insure that the function is defined at the discontinuity.

Definition 1. For two functions ϕ, ψ defined in G_p, we denote $\phi \leqq \psi$ on R_p^+ or R_∞: $\lim_{k\to\infty} \sup[\psi(\theta_k, \xi_k) - \phi(\theta_k, \xi_k)] \geqq 0$ and for every sequence of points $(\theta_k, \xi_k) \epsilon G_p$ for which the ξ_k form a monotone decreasing sequence of numbers for which

$$R_p^+ : (\theta_k, \xi_k) \rightarrow (\bar{\theta}, \bar{\xi}) \epsilon R_p$$

$$R_\infty : ||\xi_k||_e \rightarrow \infty \; (k \rightarrow \infty)$$

Next, we rewrite Equations (1) and (2) as

$$P_1\alpha \equiv \frac{\partial \alpha}{\partial \theta} - f\left(\theta, \xi, \alpha, \frac{\partial \alpha}{\partial \xi}, \frac{\theta^2 \alpha}{\theta \xi^2}\right) \tag{7}$$

$$P_2\beta \equiv \frac{\partial \beta}{\partial \theta} - g\left(\theta, \xi, \beta, \frac{\partial \beta}{\partial \xi}, \frac{\partial^2 \beta}{\partial \xi^2}\right) \tag{8}$$

where $f = \partial^2\alpha/\partial\xi^2 - \Gamma\alpha\beta$, $g = \Delta\, \partial^2\beta/\partial\xi^2 - \alpha\beta$ are monotonically increasing with $\partial^2\alpha/\partial\xi^2$ and $\partial^2\beta/\partial\xi^2$, respectively; moreover, $f \epsilon D(f)$ and $g \epsilon D(g)$ with $D(f)$ and $D(g)$ being suitably chosen regions in the domains of f and g

$$D(f) = \left\{ 0 < \theta < T, 0 < \xi < \infty, 0 < \alpha < 1, -\infty < \frac{\partial \alpha}{\partial \xi} < \infty, -\infty < \frac{\partial^2 \alpha}{\partial \xi^2} < \infty \right\}$$

$$D(g) = \left\{ 0 < \theta < T, 0 < \xi < \infty, 0 < \beta < 1, -\infty < \frac{\partial \beta}{\partial \xi} < \infty, -\infty \frac{\partial^2 \beta}{\partial \xi^2} < \infty \right\}$$

Before we state the Nagumo Lemma (Walter, 1970) we introduce three more definitions.

Definition 2. The class E consists of all functions $\omega(\theta, \rho)$ defined in $(0, T) \times \{\rho \geqq 0\}$ with the property: for every $\tau > 0$, there is a number $\delta > 0$ and a function $\rho(\theta)$ continuous in $[0, T]$, differentiable in $(0, T]$, such that $0 < \rho(\theta) \leqq \tau$ in $(0, T]$ and

$$\frac{d\rho}{d\theta} > \omega(\theta, \rho), \rho(\theta) \geqq \delta \quad \text{in} \quad (0, T]$$

Definition 3. The function $\phi(\theta, \xi)$ belongs to the class Z_0 if it is defined and continuous in G_p. $\partial\phi/\partial\theta$ as well as the continuous derivatives $\partial\phi/\partial\xi$ and $\partial^2\phi/\partial\xi^2$ are in G_p. Further, suppose for any given f which is monotonically increasing in $\partial^2\alpha/\partial\xi^2$, $(\theta, \xi, \alpha, \partial\alpha/\partial\xi, \partial^2\bar{\alpha}/\partial\xi^2) \epsilon D(f)$ for $(\theta, \xi) \epsilon G_p$, then $\phi \epsilon Z_0(f)$.

Definition 4. The class $Z_0(g, R_n)$ includes all functions $\phi(\theta, \xi) \epsilon Z_0(g)$ which are defined and continuous in $G_p U R_n$ and have an outer normal derivative at the points of R_n.

Lemma 1. Suppose that f in (7) is monotonically increasing in $\partial^2\alpha/\partial\xi^2$ and the function v, $w \epsilon Z_0(f)$. There also exists an $\omega \epsilon E$ such that

$$\Delta f = f\left(\theta, \xi, w + \rho, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) - f\left(\theta, \xi, w, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \leqq \omega(\theta, \rho); \quad \rho \geqq 0$$

and

$$\left(\theta, \xi, w + \rho, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \epsilon D(f)$$

Suppose

(i) $v \leqq w$ on R_p^+ and on R_∞

(ii) $$\frac{\partial v}{\partial \theta} - f\left(\theta, \xi, v, \frac{\partial v}{\partial \xi}, \frac{\partial^2 v}{\partial \xi^2}\right) \leqq \frac{\partial w}{\partial \theta} - f\left(\theta, \xi, w, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \quad \text{in} \quad G_p$$

then $v \leqq w$ in G_p.

Lemma 2. Suppose that g in (8) is monotonically increasing in $\partial^2\beta/\partial\xi^2$, and the functions v, $w \epsilon Z_0(g, R_n)$. There also exists an $\omega \epsilon E$ such that

$$\Delta g = g\left(\theta, \xi, w + \rho, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) - g\left(\theta, \xi, w, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \leqq \omega(\theta, \rho); \quad \rho \geqq 0$$

and

$$\left(\theta, \xi, w + \rho, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \epsilon D(g)$$

Suppose

(i) $v \leq w$ on $(R_p - R_n)^+$ and R_∞, $\frac{\partial v}{\partial \xi} \leq \frac{\partial w}{\partial \xi}$ on R_n

(ii) $$\frac{\partial v}{\partial \theta} - g\left(\theta, \xi, v, \frac{\partial v}{\partial \xi}, \frac{\partial^2 v}{\partial \xi^2}\right) \leq \frac{\partial w}{\partial \theta} - g\left(\theta, \xi, w, \frac{\partial w}{\partial \xi}, \frac{\partial^2 w}{\partial \xi^2}\right) \quad \text{in} \quad G_p$$

then $v \leq w$ in G_pUR_n. To construct the upper solution to β, we consider

$$\frac{\partial \tilde{\beta}}{\partial \theta} = \Delta \frac{\partial \tilde{\beta}^2}{\partial \xi^2} \tag{9}$$

$$\tilde{\beta}(\xi, 0) = 1, \quad \frac{\partial \tilde{\beta}}{\partial \xi}(0, \theta) = 0, \quad \tilde{\beta}(\infty, \theta) = 1 \tag{10}$$

The solution to (9) and (10) can be obtained by taking the Laplace transformation with respect to θ to obtain $\tilde{\beta} = 1$. We notice that

$$\Delta g = g\left(\theta, \xi, \tilde{\beta} + \rho, \frac{\partial \tilde{\beta}}{\partial \xi}, \frac{\partial^2 \tilde{\beta}}{\partial \xi^2}\right) - g\left(\theta, \xi, \tilde{\beta}, \frac{\partial \tilde{\beta}}{\partial \xi}, \frac{\partial^2 \tilde{\beta}}{\partial \xi^2}\right)$$
$$= -\alpha\rho \equiv \omega(\theta, \rho)$$

Noting that $P_2\tilde{\beta} < 0$ and since $d\rho/d\theta > -\alpha\rho$ implies that $\rho(\theta) > e^{-\alpha\rho} > e^{-\tau}$ for $\rho < \tau$, by choosing $\delta = e^{-\tau}$ for given $\tau > 0$, it can be shown that ω satisfies all the requirements of E, therefore $\omega \epsilon E$. Since $\tilde{\beta}$ satisfies all the requirements of Lemma 2, we have $\beta \leq \tilde{\beta} = 1$. The lower solution to β is given by the solution of

$$\frac{\partial \bar{\beta}}{\partial \theta} = \Delta \frac{\partial^2 \bar{\beta}}{\partial \xi^2} - \bar{\beta} \tag{11}$$

$$\bar{\beta}(\xi, 0) = 1, \quad \frac{\partial \bar{\beta}}{\partial \xi}(0, \theta) = 0, \quad \bar{\beta}(\infty, \theta) = e^{-\theta} \tag{12}$$

namely, $\bar{\beta} = e^{-\theta}$. The same procedure described earlier for $\tilde{\beta}$ can be applied to show that $\bar{\beta} \leq \beta$.

The lower solution of α is provided by the solution of

$$\frac{\partial \bar{\alpha}}{\partial \theta} = \frac{\partial^2 \bar{\alpha}}{\partial \xi^2} - \Gamma\bar{\alpha} \tag{13}$$

$$\bar{\alpha}(\xi, 0) = 0, \quad \bar{\alpha}(0, \theta) = 1, \quad \bar{\alpha}(\infty, \theta) = 0 \tag{14}$$

given by Carslaw and Jaeger (1959);

$$\bar{\alpha} = \frac{1}{2}\left\{ e^{-\xi\sqrt{\Gamma}}\text{erfc}\left(\frac{\xi}{2\sqrt{\theta}} - \sqrt{\Gamma\theta}\right) + e^{\xi\sqrt{\Gamma}}\text{erfc}\left(\frac{\xi}{2\sqrt{\theta}} + \sqrt{\Gamma\theta}\right)\right\} \tag{15}$$

Since $P_1\bar{\alpha} < 0$, and we have

$$\Delta f = f\left(\theta, \xi, \bar{\alpha} + \rho, \frac{\partial \bar{\alpha}}{\partial \xi}, \frac{\partial^2 \bar{\alpha}}{\partial \xi^2}\right) - f\left(\theta, \xi, \bar{\alpha}, \frac{\partial \bar{\alpha}}{\partial \xi}, \frac{\partial^2 \bar{\alpha}}{\partial \xi^2}\right)$$
$$= -\Gamma\beta\rho \equiv \omega(\theta, \rho); \quad \rho \geq 0$$

where $d\rho/d\theta > -\Gamma\beta\rho$ implies that $\rho > e^{-\Gamma\beta\rho} > e^{-\Gamma\tau}$ for $\rho < \tau$. Choosing $\delta = e^{-\Gamma\tau}$ for any given $\tau > 0$, we have $\omega \epsilon E$. By Lemma 1, we conclude that $\bar{\alpha} \leq \alpha$. Suppose we are given

$$\frac{\partial \tilde{\alpha}}{\partial \theta} = \frac{\partial^2 \tilde{\alpha}}{\partial \xi^2} - \Gamma\tilde{\alpha}e^{-\theta} \tag{16}$$

$$\tilde{\alpha}(\xi, 0) = 0, \quad \tilde{\alpha}(0, \theta) = 1, \quad \tilde{\alpha}(\infty, \theta) = 0 \tag{17}$$

Introducing the change of variable $\tilde{\alpha} = ve^{\Gamma e^{-\theta}}$, (16) and (17) become

$$\frac{\partial v}{\partial \theta} = \frac{\partial^2 v}{\partial \xi^2} \tag{18}$$

$$v(\xi, 0) = 0, \quad v(0, \theta) = h(\theta) = e^{-\Gamma e^{-\theta}}, \quad v(\infty, \theta) = 0 \tag{19}$$

By Duhamel's theorem, we can show that the solution to (18) and (19) is (Carslaw and Jaeger, 1959)

$$v = \frac{\xi}{2\sqrt{\pi}} \int_0^\theta h(\lambda) \exp(-\xi^2/4(\theta - \lambda))/(\theta - \lambda)^{3/2} d\lambda$$

or

$$\tilde{\alpha} = \frac{2\exp(\Gamma e^{-\theta})}{\sqrt{\pi}} \int_{\frac{\xi}{2\sqrt{\theta}}}^\infty h\left(\theta - \frac{\xi^2}{4\mu^2}\right) e^{-\mu^2} d\mu \tag{20}$$

The same arguments for $\bar{\alpha}$ can be employed for $\tilde{\alpha}$ to show that $\alpha \leq \tilde{\alpha}$. To sum up, we have $e^{-\theta} \leq \beta \leq 1$ and $\bar{\alpha} \leq \alpha \leq \tilde{\alpha}$, where $\bar{\alpha}$ and $\tilde{\alpha}$ are defined by (15) and (20).

CONCLUSION

We note that the function h in (20) is bounded by

$$h\left(\theta - \frac{\xi^2}{4\mu^2}\right) = \exp\left(-\Gamma e^{-\theta} e^{\frac{\xi^2}{4\mu^2}}\right) \leq e^{-\Gamma} \quad \text{for} \quad \frac{\xi}{2\sqrt{\theta}} \leq \mu \leq \infty$$

Hence (21) can be simplified to

$$\alpha \leq \frac{2\exp(\Gamma e^{-\theta})}{\sqrt{\pi}} e^{-\Gamma} \int_{\frac{\xi}{2\sqrt{\theta}}}^\infty e^{-\mu^2} d\mu$$
$$= \exp[-\Gamma(1 - e^{-\theta})]\text{erfc}\left(\frac{\xi}{2\sqrt{\theta}}\right) \tag{21}$$

When Γ is very small, α is then bounded above by erfc $(\xi/2\sqrt{\theta})$ which is the same as (5). We also note that the lower bound given by (15) is identical to (6). We conclude that our results are in accord with Pearson's physical reasoning. However, it should be noted that (6) only holds for $\Gamma >> 1$, while (15) holds for all values of Γ. Thus our constructed bounds offer an advantage over Pearson's asymptotic solutions. Hence, further application of the Nagumo Lemma will undoubtedly enhance our understanding of nonlinear equations.

NOTATION

α = dimensionless variable of the concentration of species A

β = dimensionless variable of the concentration of species B

$\underset{\sim}{\alpha}, \tilde{\alpha}$ = lower and upper solutions of α

$\bar{\beta}, \tilde{\beta}$ = lower and upper solutions of β

θ = dimensionless variable of time

ξ = dimensionless variable of the spatial coordinate x

Δ = ratio of the coefficient of diffusion of species A to the coefficient of diffusion of species B

Γ = ratio of the concentration of species B at $t = 0$ to the concentration of species A at $x = 0$

G_p, R_p = domain and boundary of systems (1) and (2)

R_n = subset of R_p

R_p^+, R_∞ = boundary, defined in definition 1

θ_k, ξ_k = sequences of θ and ξ, defined in definition 1

ϕ, ψ = functions defined in G_p, see definition 1

$||\xi_k||_e$ = Euclidean distance

f, g = functions, defined by (7) and (8)

$D(f), D(g)$ = domains of f and g

ρ = function, defined in definition 2

τ, δ = small number, defined in definition 2

T = some large dimensionless variable of time

$Z_0(f), Z_0(g, R_n)$ = function class, defined in definitions 3 and 4

h = function, defined by (19)

P_1, P_2 = differential operators, defined in (7) and (8)

U = union, set notation

ϵ = element of, set notation

$\subset$ = subset of, set notation

E = function class, defined in definition 2

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Prediction of Partial Molar Volume from the Lee-Kesler Equation of State

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Based on Pitzer's three-parameter corresponding states principles (1955), Lee and Kesler (1975) developed an analytical method to represent the thermodynamic function of any fluid F in terms of a simple fluid contribution $F^{(o)}$ and of a reference fluid contribution $F^{(r)}$ as follows:

$$F = F^{(o)} + \frac{\omega}{\;} [F^{(r)} - F^{(o)}] \tag{1}$$

The function for both the simple fluid $F^{(o)}$ and the reference fluid $F^{(r)}$ are derived from a reduced form of the modified BWR equation of state with a different set of constants:

$$Z = \left(\frac{P_r V_r}{T_r}\right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{C_4}{T_r^3 V_r^3}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \tag{2}$$

where

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \tag{3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \tag{4}$$

$$D = d_1 + \frac{d_2}{T_r} \tag{5}$$

and b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, β, and γ are constants.

The set of constants for the simple fluid are determined from the data for argon, krypton, and methane and that of the reference fluid are from the data for n-octane. The Lee-Kesler correlation is accurate in estimating thermodynamic properties for nonpolar fluids (Reid et al., 1977; Danner et al., 1976). In this work, the Lee-Kesler equation of state is applied in the calculation of the partial molar volumes of nonpolar binary mixtures.

METHOD OF CALCULATION

If the thermodynamic function F in Equation (1) is the compressibility factor, then Equation (1) can be written as

$$Z = Z^{(o)} + \frac{\omega}{\omega^{(r)}} [Z^{(r)} - Z^{(o)}] \tag{6}$$

From the definition, $Z = Pv/RT$, $Z^{(o)} = P_r V_r^{(o)}/T_r$, and $Z^{(r)} = P_r V_r^{(r)}/T_r$, we obtain

$$v = \frac{RT}{P}\left\{ \frac{P_r}{T_r}\left[V_r^{(o)} + \frac{\omega}{\omega^{(r)}} (V_r^{(r)} - V_r^{(o)}) \right] \right\} \tag{7}$$