STEADY STATE MULTIPLICITY FOR TWO CONSECUTIVE OR ISOLATED PARALLEL FIRST ORDER REACTIONS.

A Dissertation

Presented to

the Faculty of the Chemical Engineering Department

University of Houston

Houston, Texas

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

by

Constantine Andrew Pikios

December 1977

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ABSTRACT

This work examines and classifies the steady state behavioral features of lumped parameter systems in which either two consecutive first order chemical reactions $A \rightarrow B \rightarrow C$, or two independent first order chemical reactions $A \rightarrow P_1$, $B \rightarrow P_2$ occur. Both reaction schemes behave in a similar fashion, and it is shown that the case of $A \rightarrow P_1$, $B \rightarrow P_2$ can be treated as a special case of $A \rightarrow B \rightarrow C$. When both reactions are endothermic, a unique steady state solution exists. When both reactions are exothermic, a maximum of five steady state solutions could occur. When one reaction is exothermic and the other is endothermic a maximum of three steady state solutions may exist. When one reaction is isothermal and the other is endothermic a unique solution exists, while when both reactions are isothermal y=1 is the only steady state solution. When the first reaction is exothermic and the second is isothermal, the problem degenerates to that of a single chemical reaction occuring in a lumped parameter system. However, when the first reaction is isothermal and the second is exothermic, a maximum of five steady state solutions may occur.

Sufficient conditions for uniqueness and multiplicity have been derived for each subcase. The existence of steady state multiplicity over an unbounded range of Damkohler numbers has been confirmed. For certain sets of parametric

values multiplicity could occur for ALL values of Da_2, when both reactions are exothermic. For the first time, sufficient conditions for the existence of FIVE steady state solutions have been derived for the case of two exothermic reactions. Various forms of the steady state equation have been analyzed yielding sufficient conditions for multiplicity, which are much simpler than those previously reported in the literature.

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CHAPTER I

INTRODUCTION

The occurence of steady state multiplicity in lumped parameter systems is well documented [1] and plays an important role in the design, start-up and control of chemical reactors. Certain unexpected phenomena such as hysteresis of the steady state temperature of the reactor with changing feed temperatures [2], and situations in which a "runaway" occurs as the rate of some undesired reaction becomes important have been observed in industrial applications and they are due to the existence of multiple steady states.

Such pathological behavior in the operation of chemical reactors necessitates knowledge of the conditions under which steady state uniqueness and multiplicity occurs in lumped parameter systems. For the case of a single chemical reaction, necessary and sufficient conditions for the existence of a unique solution have already been derived [3-5], and it has been shown [6] that for reaction systems with kinetic expressions satisfying some liberal restrictions an odd number of multiple steady state solutions exists. These results apply to continuous stirred tank reactors, non-porous catalytic pellets and catalytic wires.

Due to the difficulty involved in deriving uniqueness and multiplicity criteria for lumped parameter systems in which

several chemical reactions occur simultaneously [7-11], few such studies have been reported in the chemical engineering literature [12-13], eventhough there is an extensive knowledge of other related topics in reaction engineering [14-16].

In a pioneering work [12] Chen and Luss developed sufficient conditions for uniqueness and multiplicity of the steady state solutions of lumped parameter systems in which two parallel first order chemical reactions occur. Several surprising and new features were found such as the occurence of multiple solutions for two parallel endothermic reactions and the existence of steady state multiplicity over an unbounded range of Damkohler numbers. Also, the numerical examples indicate that the interaction between the chemical and transport rate processes can turn an undesired reaction, whose rate is negligible at the ambient conditions, into the controlling one. These surprising results led to the conclusion that it is very dangerous to predict the qualitative behavior of a system in which a complex reaction network occurs from an analysis of a simplified reaction scheme. Since in industrial applications problems caused by steady state multiplicity are of

potential importance mainly for complex reaction networks, it is imperative that the special behavioral features of these networks be understood in order to avoid errors in design and operation. Michelsen [13] derived (for a certain range of dimensionless heat of reactions) uniqueness and multiplicity criteria which are stronger and easier to apply than those derived by Chen and Luss [12].

Many behavioral features of lumped and distributed parameter models are often similar. Thus, the analysis of lumped models should be at least indicative of the trends which we expect to observe for distributed parameter models. It should be emphasized, that a distributed parameter model of a complex reaction network is more realistic and complicated than the corresponding lumped one, because it also accounts for intra-particle gradients, and that there are mathematical techniques for transforming a distributed parameter model of a porous catalytic pellet into a lumped resistances model [17-18]. Andersen and Michelsen [19] were able to develop multiplicity criteria for two parallel first order chemical reactions occuring in a catalytic pellet employing a mathematical model which accounted for diffusion. They found that the criteria developed for the lumped parameter model [13] could be applied to the distributed parameter model also [19].

A logical extension of [12] is to derive uniqueness and multiplicity criteria for other lumped systems with complex reaction schemes, such as $A \rightarrow B \rightarrow C$ or $A \rightarrow P_1$, $B \rightarrow P_2$. Numerical

studies of steady state multiplicity for the case of two first order consecutive exothermic reactions $A \rightarrow B \rightarrow C$ occuring in a continuous stirred tank reactor have been presented in [20-22]. Unfortunately, no criteria are available for a priori prediction of steady state uniqueness and multiplicity either for $A \rightarrow B \rightarrow C$ or $A \rightarrow P_1$, $B \rightarrow P_2$.

We aim to present in this work simple uniqueness and multiplicity criteria for lumped parameter systems in which two consecutive irreversible first order chemical reactions occur; as well as to show that the same criteria also apply for two completely independent irreversible first order chemical reactions. This last fact allows us to develop in a compact fashion a uniqueness and multiplicity analysis, which is applicable to homogeneous continuous stirred tank reactors, non-porous catalytic pellets and catalytic wires, wherein either one of the above-mentioned complex reaction networks occurs.

Numerous reactions of industrial importance can be represented by the two consecutive irreversible first order chemical reactions $A \rightarrow B \rightarrow C$. Examples are the partial and complete oxidation of napthalene

napthalene $\longrightarrow$ phthalic anhydride $\longrightarrow CO_2$, H_2O, the oxidation of cyclohexane

cyclohexane $\longrightarrow$ cyclohexanol $\longrightarrow$ cyclohexanone, catalytic purification reactions such as the removal of diolefins and acetylenes from olefin streams, the removal of sulfur compounds

from hydrocarbon streams, and various halogenation reactions. All these reactions can be assumed to be of pseudo-first order, if one reactant is used in large excess. In general, the two consecutive rections may not be first order; nevertheless, the behavior of a series of first order reactions should be indicative of the features encountered in higher order systems and many industrially important reactions are well represented by this reaction scheme.

Examples of two completely indepented irreversible first order chemical reactions include the hydrodesulfurization of organic sulfur compounds $R_1SH \longrightarrow R_1H + H_2S$, $R_2SH \longrightarrow R_2H + H_2S$, and various poisoning mechanisms $A \longrightarrow P_1$, $B \longrightarrow P_2$, where A and B represent components commonly found in petroleum industry feeds, with one reaction (main) occuring much faster than the other (poisoning reaction).

Our analysis is carried-out through the division of the problem into several subcases covering not only the case of two exothermic reactions [20-22], but also two endothermic as well as the case of one endothermic and one exothermic reaction. The possibility of one of the two reactions being isothermal is also examined, in order to derive uniqueness and multiplicity criteria. In addition, for each possible subcase extensive numerical calculations were performed and relevant parametric values adjusted, in order to investigate the behavior of the steady state equation and find the maximum number of possible solutions.

Hopefully, the methodology and the criteria presented in this work, as well as in previous publications [12-13], will be be useful in examining the behavioral features of more complicated chemical reaction networks such as

$$\begin{tikzcd} A \arrow[r] \arrow[dr] & B \arrow[r] & C \\ & D & \end{tikzcd}$$

[23-24] and of higher order systems [25].

CHAPTER II

DEVELOPMENT OF THE MATHEMATICAL MODEL

Consider two first order irreversible consecutive reactions

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

occuring in a porous catalytic pellet and assume that the intra-particle temperature and concentration gradients are negligible [15,26]. Then, the following steady state species and energy conservation equations apply

$$\varepsilon_p K_{ca} S_x (A_o - A_s) = V_p K_1 A_s \tag{1}$$

$$\varepsilon_p K_{cB} S_x (B_s - B_o) = V_p (K_1 A_s - K_2 B_s) \tag{2}$$

$$h S_x (T - T_o) = (-\Delta H_1) V_p K_1 A_s + (-\Delta H_2) V_p K_2 B_s \tag{3}$$

Such equations could be written for other lumped parameter systems also, in the case of two first order consecutive reactions (Appendix A).

Letting

$$K_i = K_i(T_o) * \exp\left[\frac{E_i}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right], \quad i = 1, 2 \tag{4}$$

and introducing the dimensionless variables

$$\gamma_1 = E_1 / R T_o \quad \text{(5a)}$$

$$\mu = E_2 / E_1 \quad \text{(5b)}$$

$$y = T / T_o \quad \text{(5c)}$$

$$X = \exp\left[\gamma_1 \left(1 - \frac{1}{y}\right)\right] \quad \text{(5d)}$$

$$\nu = K_{ca} / K_{cB} \quad \text{(5e)}$$

$$\mathcal{D}a_1 = \frac{V_p \; K_1(T_o)}{\varepsilon_p K_{ca} S_x} \; , \; \mathcal{D}a_2 = \frac{V_p \; K_2(T_o)}{\varepsilon_p K_{cB} S_x} \quad \text{(5f)}$$

$$\beta_1 = \frac{(-\Delta H_1) K_{ca} A_o \varepsilon_p}{h T_o} \; , \; \beta_2 = \frac{(-\Delta H_2) K_{cB} A_o \varepsilon_p}{h T_o} \quad \text{(5g)}$$

allows us to rewrite equs. (1)-(2) as

$$\left(\frac{A_s}{A_o}\right) = \frac{1}{(1 + \mathcal{D}a_1 X)} \quad \text{(6)}$$

$$\left(\frac{B_s}{A_o}\right) = \frac{1}{(1 + \mathcal{D}a_2 X^{\mu})} \left[\alpha + \frac{\nu \mathcal{D}a_1 X}{(1 + \mathcal{D}a_1 X)}\right] \quad \text{(7)}$$

where

$$\alpha = \left(B_o / A_o \right) \tag{8}$$

Using (4)-(5g) and substituting equs. (6)-(7) into (3) yields

$$(y-1) = \beta_1 \frac{\mathcal{D}_{a_1} X}{(1+\mathcal{D}_{a_1} X)} + \beta_2 \frac{\mathcal{D}_{a_2} X^{\mu}}{(1+\mathcal{D}_{a_2} X^{\mu})} \left[\alpha + \frac{\nu \mathcal{D}_{a_1} X}{(1+\mathcal{D}_{a_1} X)} \right] \tag{9}$$

For two first order irreversible completely independent chemical reactions

$$A \xrightarrow{K_1} P_1 \ , \quad B \xrightarrow{K_2} P_2$$

occuring in a porous catalytic pellet, where intra-particle temperature and concentration gradients are assumed to be negligible, one can easily show (Appendix B) that the steady state equation results from (9) by deleting the term involving ν ($\nu \equiv 0$) and requiring that $\alpha \neq 0$. Consequently, (9) embodies the following two subproblems:

Subproblem I : $\nu \neq 0$

(i) $\alpha \neq 0$:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C, \text{ where } B_0 \neq 0.$$

(ii) $\alpha = 0$:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C, \text{ where } B_0 = 0.$$

Subproblem II : $\gamma \equiv 0$, $\alpha \neq 0$

$$A \xrightarrow{K_1} P_1, \; B \xrightarrow{K_2} P_2$$

The above formulation allows for compactness in the analytical development and the use of a single steady state equation, i.e. equ. (9), for both complex reaction networks. Note that the notation $\gamma \equiv 0$ does not mean that $k_{ca}=0$: We simply delete the term containing γ in equ. (9).

CHAPTER III

DERIVATION OF UNIQUENESS AND MULTIPLICITY CRITERIA.

Subcase 3A: $\beta_1 \leq 0, \beta_2 \leq 0$

Lemma 3A1: Equation (9) has a unique steady state solution for both subproblems I and II.

Proof

(i) $\beta_1 < 0, \beta_2 < 0$ (Two endothermic reactions).

Equation (9) can be rewritten as

$$\frac{1}{\beta_1} = \frac{f_1(y)}{(y-1)} \tag{10}$$

where

$$f_1(y) \triangleq \left\{ \frac{\mathcal{D}a_1}{(\mathcal{D}a_1 + X^{-1})} + \frac{B\mathcal{D}a_2}{(\mathcal{D}a_2 + X^{-\mu})} \left[\alpha + \frac{\gamma \mathcal{D}a_1}{(\mathcal{D}a_1 + X^{-1})} \right] \right\} \tag{11}$$

$$B \triangleq (\beta_2 / \beta_1) > 0 \tag{12}$$

Suppose that y_1, y_2 are two distinct solutions of (10).

Then,

$$(y_1 - 1) = \beta_1 f_1(y_1) \tag{13a}$$

$$(y_2 - 1) = \beta_1 f_1(y_2) \tag{13b}$$

Subtracting (13b) from (13a) yields

$$U \triangleq (y_1 - y_2) = \beta_1 \left[f_1(y_1) - f_1(y_2) \right] \tag{14}$$

Using the mean-value theorem allows to rewrite (14) as [5]

$$U = \beta_1 U f_1'(y^{\Delta}) \tag{15}$$

where $y^{\Delta} \in (y_1, y_2)$.

From (11) it follows that for both subproblems I and II

$$f_1'(y) > 0 \tag{16}$$

because

$$f_1'(y) = \frac{\mathcal{D}a_1 X^{-1}(\gamma_1/y^2)}{(\mathcal{D}a_1 + X^{-1})} + \frac{B\alpha \mathcal{D}a_2 X^{-\mu}(\mu\gamma_1/y^2)}{(\mathcal{D}a_2 + X^{-\mu})^2} +$$

$$+ \frac{B\gamma \mathcal{D}a_1 \mathcal{D}a_2 (\gamma_1/y^2)\left[\mathcal{D}a_2 X^{-1} + \mu \mathcal{D}a_1 X^{-\mu} + (\mu+1) X^{-(\mu+1)}\right]}{(\mathcal{D}a_1 + X^{-1})^2 \, (\mathcal{D}a_2 + X^{-\mu})^2} \tag{16a}$$

Consequently, (15) is contradicted since $\beta_1 < 0$. Therefore, uniqueness is assured for all $\beta_1 < 0$ of (10) when $B > 0$.

(ii) $\beta_1 = 0$, $\beta_2 < 0$ (One isothermal and one endothermic reaction).

Equation (9) can be rewritten as

$$\frac{1}{\beta_2} = \frac{f_2(y)}{(y-1)} \tag{17}$$

where

$$f_2(y) \triangleq \frac{\mathcal{D}a_2}{(\mathcal{D}a_2 + X^{-\mu})}\left[\alpha + \frac{\nu\,\mathcal{D}a_1}{(\mathcal{D}a_1 + X^{-1})}\right] \tag{17a}$$

Again, we can prove that $f_2'(y) > 0$, and repeating the same procedure as in (i) we conclude that for both subproblems uniqueness is assured for all $\beta_2 < 0$ of (17) when $\beta_1 = 0$.

(iii) $\beta_1 < 0$, $\beta_2 = 0$ (One endothermic and one isothermal reaction).

Equation (9) becomes

$$(y-1) = \beta_1 \frac{\mathcal{D}a_1 X}{(1 + \mathcal{D}a_1 X)} \tag{18}$$

Equ. (18) is the steady state equation for a single chemical reaction occuring in a lumped parameter system, and since $\beta_1 < 0$ uniqueness is assured for all Da_1 [12].

(iv) $\beta_1 = \beta_2 = 0$ (Two isothermal reactions).

From (9) it follows that y=1 is the only steady state solution for both subproblems I and II.

Subcase 3B: $\beta_1 \geqslant 0$, $\beta_2 > 0$ or $\beta_1 > 0$, $\beta_2 = 0$.

For $\beta_1 > 0$, $\beta_2 = 0$, equ. (9) yields (18). Uniqueness and multiplicity criteria have already been derived [3] for (18) when $\beta_1 > 0$, and we know that a maximum of three steady state solutions could occur.

Lemma 3B1: Suppose that $\beta_1 \geqslant 0$, $\beta_2 > 0$. Let Da_1 be such that $1 \leqslant y^{**} < (1+\beta_1)$ is the only root of the equation

$$[(y-1) - \mathcal{D}a_1 \mathbb{X}(1+\beta_1 - y)] = 0 \tag{19}$$

and

$$(1+\alpha\beta_2) < y^* < [1+\beta_1+(\gamma+\alpha)\beta_2]$$

denote the largest root of the equation

$$(1+\alpha\beta_2 - y) + \mathcal{D}a_1 \mathbb{X}[1+\beta_1+(\gamma+\alpha)\beta_2 - y] = 0 \tag{20}$$

Then, a necessary and sufficient condition for uniqueness for all Da_2 of the steady state equation

$$\frac{1}{\mathcal{D}a_2} = \frac{\mathbb{X}^{\mu}\{(1+\alpha\beta_2 - y) + \mathcal{D}a_1 \mathbb{X}[1+\beta_1+(\gamma+\alpha)\beta_2 - y]\}}{[(y-1) - \mathcal{D}a_1 \mathbb{X}(1+\beta_1 - y)]} \triangleq F(y) \tag{21}$$

is [3] that

$$dF(y)/dy < 0 \quad , \text{ where } y^{**} < y < y^* \tag{22}$$

Derivation of uniqueness criteria using Lemma 3B1.

Equs. (21)-(22) yield

$$\beta_2 y^2+\mu\gamma_1(y-1)\Theta(y)\left\{(y-1)-\left[\alpha\beta_2+h_1(y)+h_2(y)\right]\right\}+\mu\gamma_1\beta_1 M(y)>0 \qquad (23)$$

$$y\in(y^{**},y^{*})$$

where

$$\Theta(y)\triangleq\frac{1}{\left[\alpha+\frac{\gamma\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}\right]}>0 \qquad (24a)$$

$$h_1(y)\triangleq\frac{(2\beta_1+\gamma\beta_2)}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)}>0 \qquad (24b)$$

$$h_2(y)\triangleq\frac{\gamma\beta_2\mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)^2}>0 \qquad (24c)$$

$$M(y)\triangleq\frac{\mu\mathcal{D}a_1^2 X^2\left[\beta_1+(\gamma+\alpha)\beta_2\right]+(\mu-1)\alpha\beta_2\mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)\left[\alpha(1+\mathcal{D}a_1 X)+\gamma\mathcal{D}a_1 X\right]} \qquad (24d)$$

For (23) to hold it suffices that

$$\beta_2 y^2+\mu\gamma_1(y-1)\bar{\theta}\left[(y-1)-\left(\alpha\beta_2+\bar{h}_1+\bar{h}_2\right)\right]+\mu\gamma_1\beta_1\underline{M}>0 \qquad (25)$$

$$y\in(y^{**},y^{*})$$

where

$$\bar{\theta}\triangleq\max_{y^{**}<y<y^{*}}\theta(y)=\theta(y^{**})\leq\theta(1)\triangleq\frac{1}{\left[\alpha+\frac{\nu\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]} \qquad (26a)$$

$$\bar{h}_1\triangleq\max_{y^{**}<y<y^{*}}h_1(y)=h_1(y^{*})\leq h_1\left(1+\beta_1+(\nu+\alpha)\beta_2\right)<\left(2\beta_1+\nu\beta_2\right) \qquad (26b)$$

$$\bar{h}_2\triangleq\max_{y^{**}<y<y^{*}}h_2(y)<\left(\frac{\nu\beta_2}{4\mu}\right) \qquad (26c)$$

$$\underline{M}\triangleq\min_{y^{**}<y<y^{*}}M(y)=M(y^{**})\geqslant M(1)=$$

$$=\frac{\mu\mathcal{D}a_1^2\left[\beta_1+(\nu+\alpha)\beta_2\right]+(\mu-1)\alpha\beta_2\mathcal{D}a_1}{\mu(1+\mathcal{D}a_1)\left[\alpha+(\nu+\alpha)\mathcal{D}a_1\right]} \qquad (26d)$$

For the derivation of (26c)-(26d) see Appendix C.

Condition (25) can be rewritten as

$$(\beta_2+\mu\gamma_1\bar{\theta})y^2-\mu\gamma_1\bar{\theta}(2+\alpha\beta_2+\bar{h}_1+\bar{h}_2)y+$$

$$+\mu\gamma_1[\bar{\theta}(1+\alpha\beta_2+\bar{h}_1+\bar{h}_2)+\beta_1\underline{M}]>0 \qquad (27)$$

$$y\in(y^{**},y^{*})$$

For (27) to hold it suffices that

$$\mu\gamma_1\bar{\theta}^2(2+\alpha\beta_2+\bar{h}_1+\bar{h}_2)^2<4(\beta_2+\mu\gamma_1\bar{\theta})*$$

$$*[\bar{\theta}(1+\alpha\beta_2+\bar{h}_1+\bar{h}_2)+\beta_1\underline{M}] \qquad (28)$$

From (24a)-(24d) we see that when $Da_1=0$, (28) reduces to

$$\mu\gamma_1(\alpha\beta_2)<4(1+\alpha\beta_2)$$

Substituting (26a)-(26d) into (28) yields

$$\mu\gamma_1\eta_1^2<4\left[\alpha+\frac{\gamma\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]*$$

$$*\left\{\mu\gamma_1\beta_1\underline{M}+\beta_2\left[(1-\eta_1)+\beta_1\underline{M}\left[\alpha+\frac{\gamma\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]\right]\right\} \qquad (29)$$

where

$$\eta_1 \triangleq -2\beta_1 - \beta_2\left[\alpha + \nu\left(1 + \frac{1}{4\mu}\right)\right] \tag{30}$$

and $\underline{M}$ is given by (26d).

Condition (29) is a sufficient condition for uniqueness for all values of Da_2 of the steady state equation (21) in the case of subproblem I(i) when $\beta_1 > 0$, $\beta_2 > 0$.

For subproblem I(ii), (29) yields

$$\mu\gamma_1\eta_2^2 < 4\frac{\nu\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\left\{\frac{\mu\gamma_1\beta_1\mathcal{D}a_1(\beta_1+\nu\beta_2)}{\nu(1+\mathcal{D}a_1)} + \right.$$

$$\left. + \beta_2\left[(1-\eta_2) + \beta_1\left(\frac{\mathcal{D}a_1}{1+\mathcal{D}a_1}\right)^2(\beta_1+\nu\beta_2)\right]\right\} \tag{31}$$

where

$$\eta_2 \triangleq -2\beta_1 - \nu\beta_2\left(1 + \frac{1}{4\mu}\right) \tag{31a}$$

For subproblem II, (29) yields

$$\mu\gamma_1\eta_3^2 < 4\alpha\left\{\beta_2(1-\eta_3) + \beta_1(\mu\gamma_1 + \alpha\beta_2) * \right.$$

$$\left. * \frac{[\mu\mathcal{D}a_1^2(\beta_1+\alpha\beta_2) + (\mu-1)\alpha\beta_2\mathcal{D}a_1]}{\mu\alpha(1+\mathcal{D}a_1)^2}\right\} \tag{32}$$

where

$$\eta_3 \triangleq -\left(2\beta_1 + \alpha\beta_2\right) \tag{32a}$$

For subproblem I(ii), we could have used the steady state equation

$$\frac{1}{\mathcal{D}a_1} = \frac{X\left\{(1+\beta_1-y) + \mathcal{D}a_2 X^{\mu}\left[1+\beta_1+(\gamma+\alpha)\beta_2 - y\right]\right\}}{\left[(y-1) - \mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2 - y)\right]} \triangleq \Phi(y) \tag{33}$$

(with $\alpha = 0$) instead of (21) in order to derive the following sufficient criterion for uniqueness for all Da_1 of (33):

$$\gamma_1\left[\beta_1 + \gamma\beta_2\left(1+\frac{\mu}{4}\right)\right]^2 < 4\beta_1\left[1+\beta_1+\gamma\beta_2\left(1+\frac{\mu}{4}\right)\right] \tag{34}$$

The derivation of (34) is shown in Appendix D. (34) may be preferable to (31), since it is independent of the Damkohler numbers. Condition (34) can be rewritten in the more compact form

$$\frac{\left(\frac{\beta_1}{\lambda}\right)\gamma_1}{4\lambda\left(1+\frac{\beta_1}{\lambda}\right)} < 1 \tag{34a}$$

where

$$\lambda \triangleq \left[1+\gamma B\left(1+\frac{\mu}{4}\right)\right]^{-1} \tag{34b}$$

Observe that for $\beta_2 = 0$, (34a) reduces to the necessary and sufficient condition for uniqueness for all values of Da_1 in the case of a single chemical reaction occuring in a

lumped parameter system

$$\beta_1 \gamma_1 < 4(1+\beta_1)$$

For the parametric values

μ =2.0

B=0.5

ν =1.0

Da_2=0.10 and Da_2=0.01

α =0.0

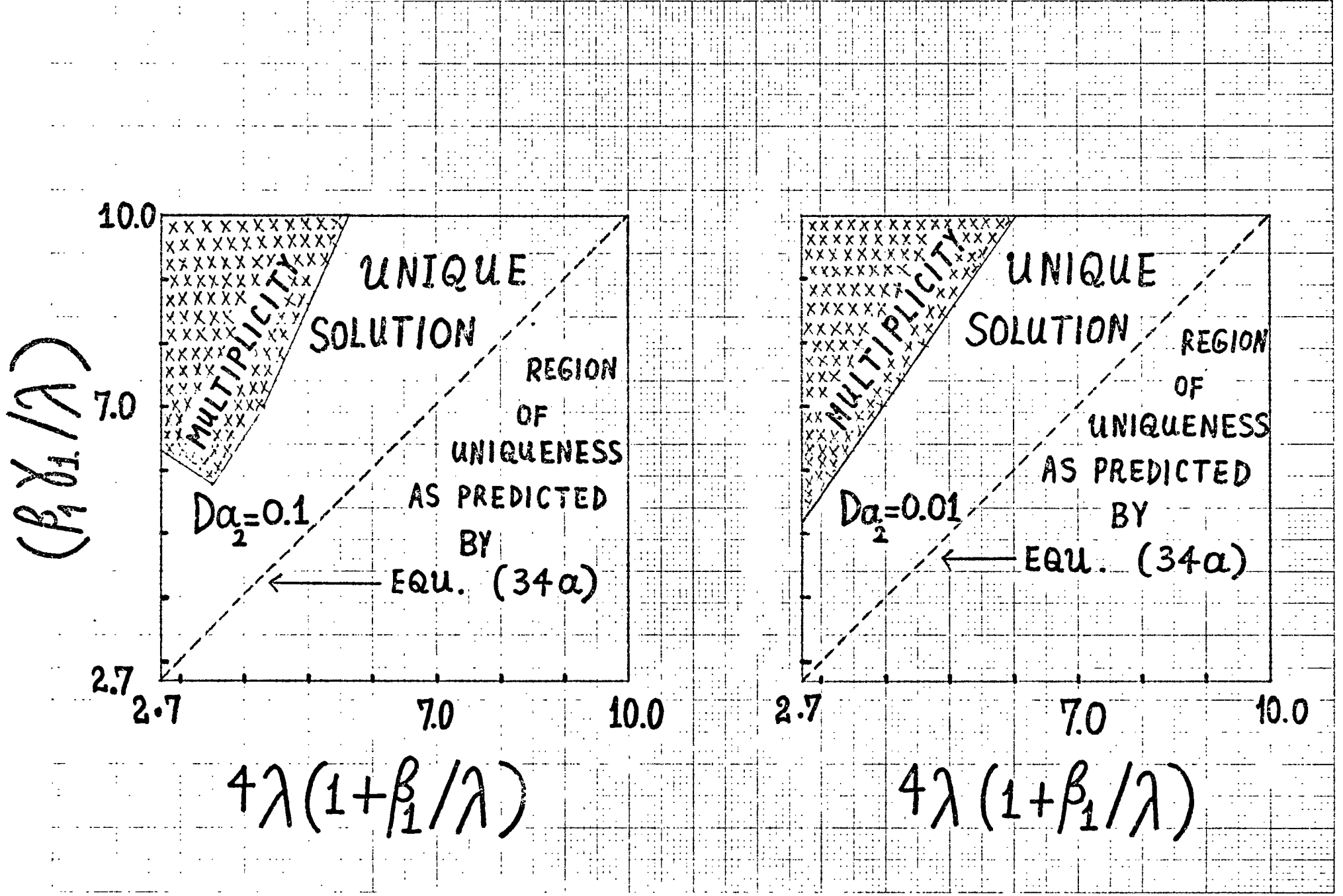
we find that λ=**0.57** and numerical use of (33) allows us to prepare a ($\beta_1\gamma_1/\lambda$) versus $4\lambda(1+\beta_1/\lambda)$ uniqueness map, in order to examine how conservative condition (34a) is for these two particular values of Da_2. Figures (1a)-(1b) present the various regions properly labeled. Clearly, (34a) is a rather conservative criterion for uniqueness.

For the special case where $\beta_1 = 0$, $\beta_2 > 0$, (29) yields the following sufficient condition for uniqueness for all Da_2 of (21) for subproblem I:

$$\frac{\mu\gamma_1(1+\eta_4)^2}{\left[\alpha+\frac{\nu \mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]} < 4\eta_4\left(\beta_2+\frac{\mu\gamma_1}{\left[\alpha+\frac{\nu \mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]}\right) \tag{35}$$

where

$$\eta_4 \triangleq 1+\beta_2\left[\alpha+\nu\left(1+\frac{1}{4\mu}\right)\right] \tag{35a}$$



Figures (1a)-(1b): Uniqueness map for two exothermic reactions in the case of subproblem I(ii).

Lemma 3B2: Simple but more conservative uniqueness criteria for both subproblems I and II can also be derived by requiring that each of the three terms on the right-hand side of the steady state equation

$$1=\frac{\mathcal{D}a_1 X(1+\beta_1-y)}{(y-1)}+\frac{\mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2-y)}{(y-1)}+\frac{\mathcal{D}a_1\mathcal{D}a_2 X^{\mu+1}[1+\beta_1+(\gamma+\alpha)\beta_2-y]}{(y-1)} \tag{36}$$

be a monotonically decreasing function of y in the interval (1, $1+\beta_1+(\gamma+\alpha)\beta_2$). Such an analysis yields the following sufficient condition for uniqueness:

$$\gamma_1 < \frac{4}{(\mu+1)}\left[1+\frac{1}{\beta_1+(\gamma+\alpha)\beta_2}\right] \tag{37}$$

See Appendix E for the proof of Lemma 3B2.

Lemma 3B3: For subproblem II, conservative criteria for uniqueness can be derived for all $\beta_1 > 0$ of equ. (10), by requiring that both terms comprising $f_1(y)$ (as defined by (11)) be monotonically decreasing functions of y ($>$ 1). For $\mu \geq 1$, the following uniqueness criteria can be derived from such an analysis:

If $\mu\gamma_1 \leq 4$, ...(38)

then uniqueness is assured for subproblem II.

If $\gamma_1 > 4$,

then the conditions

$$\mathcal{D}a_1 > \left(1-\frac{4}{\gamma_1}\right)e^{-2} \tag{39a}$$

$$\mathcal{D}a_2 > \left(1-\frac{4}{\mu\gamma_1}\right)e^{-2} \tag{39b}$$

are sufficient for uniqueness for all $\beta_1 > 0$ of (10).

If $\gamma_1 \leq 4$ and $\mu\gamma_1 > 4$, then the condition

$$\mathcal{D}a_2 > \left(1-\frac{4}{\mu\gamma_1}\right)e^{-2} \tag{40}$$

suffices for uniqueness for all $\beta_1 > 0$ of (10). The proof for Lemma 3B3 is shown in Appendix F.

Observe that Lemma 3B1 cannot be applied for the special case where $Da_1=Da_2$, because Da_1 appears on both sides of (21). The steady state equation (9) yields an algebraic equation of the second degree with respect to Da_1, from which it follows that

$$\mathcal{D}a_1 = \frac{-\left\{X(1+\beta_1-y)+\sigma X^{\mu}(1+\alpha\beta_2-y)\right\} \pm \sqrt{\left[X(1+\beta_1-y)+\sigma X^{\mu}(1+\alpha\beta_2-y)\right]^2+4\sigma X^{\mu+1}\left[1+\beta_1+(\gamma+\alpha)\beta_2-y\right](y-1)}}{2\sigma X^{\mu+1}\left[1+\beta_1+(\gamma+\alpha)\beta_2-y\right]} \tag{41}$$

where

$$\sigma \triangleq \mathcal{D}a_2 / \mathcal{D}a_1 = 1 \tag{41a}$$

Since (41) is very complicated to differentiate, it would be

preferable to use the simpler uniqueness criteria (37) or (38)-(40) when $Da_1=Da_2$.

For the rather rare case where either $\gamma_1 = 0$ or $\gamma_2 = 0$, one can see from (9) that a maximum of three steady state solutions could exist when $\beta_1 \geq 0$, $\beta_2 > 0$.

Equ. (9) can be expressed in the form (Appendix G):

$$(-\beta_2) = \frac{-\left[\frac{(y-1)}{\mathcal{D}a_1} - X(1+\beta_1-y)\right]}{\sigma\, g(y)} \triangleq Z(y) \tag{42}$$

where

$$g(y) \triangleq \left[\frac{X^{-1}+\mathcal{D}a_1}{X^{-\mu}+\mathcal{D}a_2}\right]\left[\frac{\nu X}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)}+\alpha X\right] \tag{42a}$$

Lemma 3B4: When $\beta_1 > 0$, $\beta_2 > 0$, for both subproblems I and II, a necessary and sufficient condition for uniqueness for all ($-\beta_2$) of equ. (42) is

$$dZ(y)/dy < 0, \quad 1 < y \tag{43}$$

Derivation of uniqueness criteria using condition (43)

Condition (43) can be rewritten as

$$-y^2+\gamma_1(y-1)\mathcal{H}(y)+\beta_1\gamma_1 R(y) < 0, \quad 1 < y \tag{44}$$

where

$$\mathcal{H}(y) \triangleq \frac{\mu[\alpha+(\nu+\alpha)\mathcal{D}a_1 X](1+\mathcal{D}a_1 X)+\nu\mathcal{D}a_1 X(1+\mathcal{D}a_2 X^{\mu})}{[\alpha+(\nu+\alpha)\mathcal{D}a_1 X](1+\mathcal{D}a_1 X)(1+\mathcal{D}a_2 X^{\mu})} \tag{45a}$$

$$R(y) \triangleq R_1(y) - R_2(y) \quad \cdots\cdots\cdots\cdots\cdots\cdots \tag{45b}$$

$$R_1(y) \triangleq \frac{\alpha\,\mathcal{D}a_1 X}{[\alpha+(\nu+\alpha)\mathcal{D}a_1 X](1+\mathcal{D}a_1 X)} \tag{45c}$$

$$R_2(y) \triangleq \frac{\mu\,\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)(1+\mathcal{D}a_2 X^{\mu})} \tag{45d}$$

For (44) to hold it suffices that

$$-y^2+\gamma_1(y-1)\overline{\mathcal{H}}+\beta_1\gamma_1\overline{R}_1<0\,,\ 1<y \tag{46}$$

where

$$\mathcal{H}(y) < \frac{\mu}{(1+\mathcal{D}a_2)} + \frac{\nu}{\left(1+\sqrt{\frac{\alpha}{(\nu+\alpha)}}\right)\left[\nu+\sqrt{\alpha(\nu+\alpha)}\left(1+\sqrt{\frac{\alpha}{(\nu+\alpha)}}\right)\right]} \triangleq \overline{\mathcal{H}} \tag{47a}$$

and

$$R_1(y) < \frac{\alpha}{\left(1+\sqrt{\frac{\alpha}{(\gamma+\alpha)}}\right)\left[\gamma+\sqrt{\alpha(\gamma+\alpha)}\left(1+\sqrt{\frac{\alpha}{(\gamma+\alpha)}}\right)\right]} \triangleq \bar{R}_1 \tag{47b}$$

Condition (46) can be rewritten as

$$-y^2+y\gamma_1\bar{\mathcal{H}}+\gamma_1(\beta_1\bar{R}_1-\bar{\mathcal{H}})<0\ ,\ 1<y \tag{48}$$

For (48) to hold it suffices that

$$\gamma_1\bar{\mathcal{H}}^2<4(\bar{\mathcal{H}}-\beta_1\bar{R}_1) \tag{49}$$

where $\bar{\mathcal{H}}$ and $\bar{R}_1$ are given by (47a), (47b) respectively. In the case of subproblem I(i), (49) is sufficient for uniqueness for all values of ($-\beta_2$) of the steady state equation (42) when $\beta_1>0$, $\beta_2>0$.

When $\beta_1=0$, $\beta_2>0$, condition (49) simplifies to

$$\gamma_1\bar{\mathcal{H}}<4 \tag{50}$$

OR

$$\gamma_1\left\{\frac{\mu}{(1+\mathcal{D}a_2)}+\frac{\gamma}{\left(1+\sqrt{\frac{\alpha}{(\gamma+\alpha)}}\right)\left[\gamma+\sqrt{\alpha(\gamma+\alpha)}\left(1+\sqrt{\frac{\alpha}{(\gamma+\alpha)}}\right)\right]}\right\}<4$$

For subproblem I(ii) ($\alpha = 0$), (45a)-(45b) yield

$$\mathcal{H}(y) \triangleq \frac{\mu}{(1+\mathcal{D}a_2 X^{\mu})} + \frac{1}{(1+\mathcal{D}a_1 X)} > 0 \tag{51a}$$

$$R(y) \triangleq -\frac{\mu \mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)(1+\mathcal{D}a_2 X^{\mu})} < 0 \tag{51b}$$

and for (44) to hold it suffices that

$$-y^2 + \gamma_1 (y-1)\bar{\mathcal{H}} + \beta_1 \gamma_1 \bar{R} < 0 \ , \ 1 < y \tag{52}$$

or

$$-y^2 + y\gamma_1 \bar{\mathcal{H}} + \gamma_1 (\beta_1 \bar{R} - \bar{\mathcal{H}}) < 0, \ 1 < y \tag{53}$$

where $\mathcal{H}(y) < \frac{\mu}{(1+\mathcal{D}a_2)} + \frac{1}{(1+\mathcal{D}a_1)} \triangleq \bar{\mathcal{H}}$ (54a)

$$R(y) < \begin{cases} -\dfrac{1}{\left(\dfrac{1}{\mathcal{D}a_1} + \dfrac{\mathcal{D}a_2}{\mathcal{D}a_1} + 1 + \mathcal{D}a_2 e^{\gamma_1}\right)} \triangleq \bar{R}, & \mu = 1 \\[2ex] -\dfrac{\mu}{\left(\dfrac{1}{\mathcal{D}a_1} + \dfrac{\mathcal{D}a_2}{\mathcal{D}a_1} e^{(\mu-1)\gamma_1} + 1 + \mathcal{D}a_2 e^{\mu\gamma_1}\right)}, & \mu > 1 \\[2ex] -\dfrac{\mu}{\left(\dfrac{1}{\mathcal{D}a_1} + \dfrac{\mathcal{D}a_2}{\mathcal{D}a_1} + 1 + \mathcal{D}a_2 e^{\mu\gamma_1}\right)} \triangleq \bar{R}, & \mu < 1 \end{cases} \tag{54b}$$

For (53) to hold it suffices that

$$\gamma_1 \bar{\mathcal{H}}^2 < 4\left(\bar{\mathcal{H}} - \beta_1 \bar{R}\right) \tag{55}$$

(55) is a sufficient condition for uniqueness for all values of ($-\beta_2$) of equ. (42) in the case of subproblem I(ii), when $\beta_1 > 0$, $\beta_2 > 0$. For $\beta_1 = 0$, $\beta_2 > 0$, (55) simplifies even further.

For subproblem II ($\gamma \equiv 0$), (45a)-(45b) yield

$$\mathcal{H}(y) \triangleq \frac{\mu}{(1+\mathcal{D}a_2 X^{\mu})} > 0 \tag{56a}$$

$$R(y) \triangleq R_1(y) - R_2(y) \qquad \text{.....} \tag{56b}$$

$$R_1(y) \triangleq \frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)^2} > 0$$

$$R_2(y) \triangleq -\frac{\mu\, \mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)(1+\mathcal{D}a_2 X^{\mu})} < 0$$

For (44) to hold, it suffices that (46) holds where

$$\mathcal{H}(y) < \frac{\mu}{(1+\mathcal{D}a_2)} \triangleq \bar{\mathcal{H}} \tag{57a}$$

$$R_1(y) < \frac{1}{4} \triangleq \overline{R}_1 \tag{57b}$$

Consequently, (49) can be rewritten as

$$\gamma_1 \left[\frac{\mu}{1+\mathcal{D}a_2}\right]^2 < 4\left[\frac{\mu}{(1+\mathcal{D}a_2)} - \frac{\beta_1}{4}\right] \tag{58}$$

Condition (58) suffices for uniqueness for values of ($-\beta_2$) of equ. (42) in the case of subproblem II, when $\beta_1 > 0$, $\beta_2 > 0$. When $\beta_1 = 0$, $\beta_2 > 0$, (58) simplifies even further.

This concludes our analysis on Lemma 3B4.

The results of extensive numerical calculations are presented in figures (2)-(7). Figure 2 describes five possible patterns of equ. (21) for both subproblems I and II, when F(y) has only one asymptote and both reactions are exothermic. For cases (d) and (e) a maximum of five steady state solutions could occur for some Da_2 values, despite the fact that the CSTR is not cooled as was the case in previous publications [20,27]. For case (a), a unique steady state solution exists for all Da_2, while for (b) and (c) a maximum of

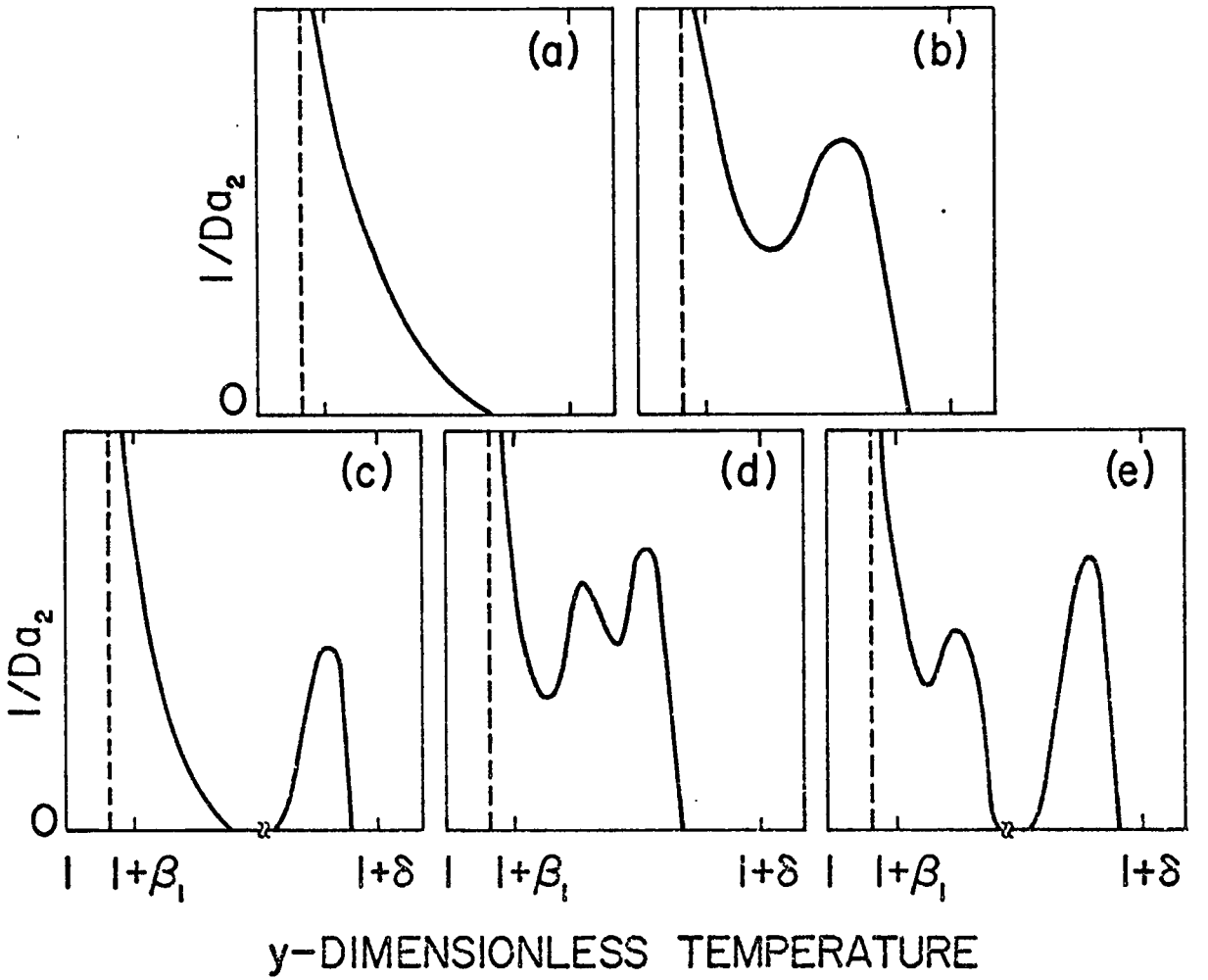


Figure 2: Various patterns of behavior for two exothermic reactions in the case of subproblems I and II.

three solutions could occur for some range of Da_2. Observe that when (19) has a unique root, then F(y) has one asymptote only.

Figure 3 describes six possible patterns of (21) for both subprobles I and II, when F(y) has two asymptotes and both reactions are exothermic. For case (a), multiplicity as a function of Da_2 is of type 3-1, and there is an upper bound on $1/Da_2$ below which uniqueness is assured. For case (b), however, (21) has three solutions for all values of Da_2. For case (c), multiplicity as a function of Da_2 is of type 3-5-3-1, and there is an upper bound on $1/Da_2$ below which uniqueness is assured. For case (d), however, multiplicity as a function of Da_2 is of type 3-5-3 and occurs for all values of Da_2. For case (e), multiplicity as a function of Da_2 is of type 3-5-3-5-3-1, and there is an upper bound on $1/Da_2$ below which uniqueness is assured. For case (f), however, multiplicity as a function of Da_2 is of type 3-5-3-5-3 and occurs for all values of Da_2.

Figure 4 describes eight possible patterns of (21) for both subproblems I and II, when F(y) has three asymptotes and the reactions are both exothermic. For figures (a)-(d), apply the same considerations as for cases (a)-(d) of figure 3. For cases (g)-(h), apply the same considerations as for cases (e)-(f) of figure 3. For case (e), multiplicity as a function of Da_2 is of type 3-5-3-1, and there is an upper bound on

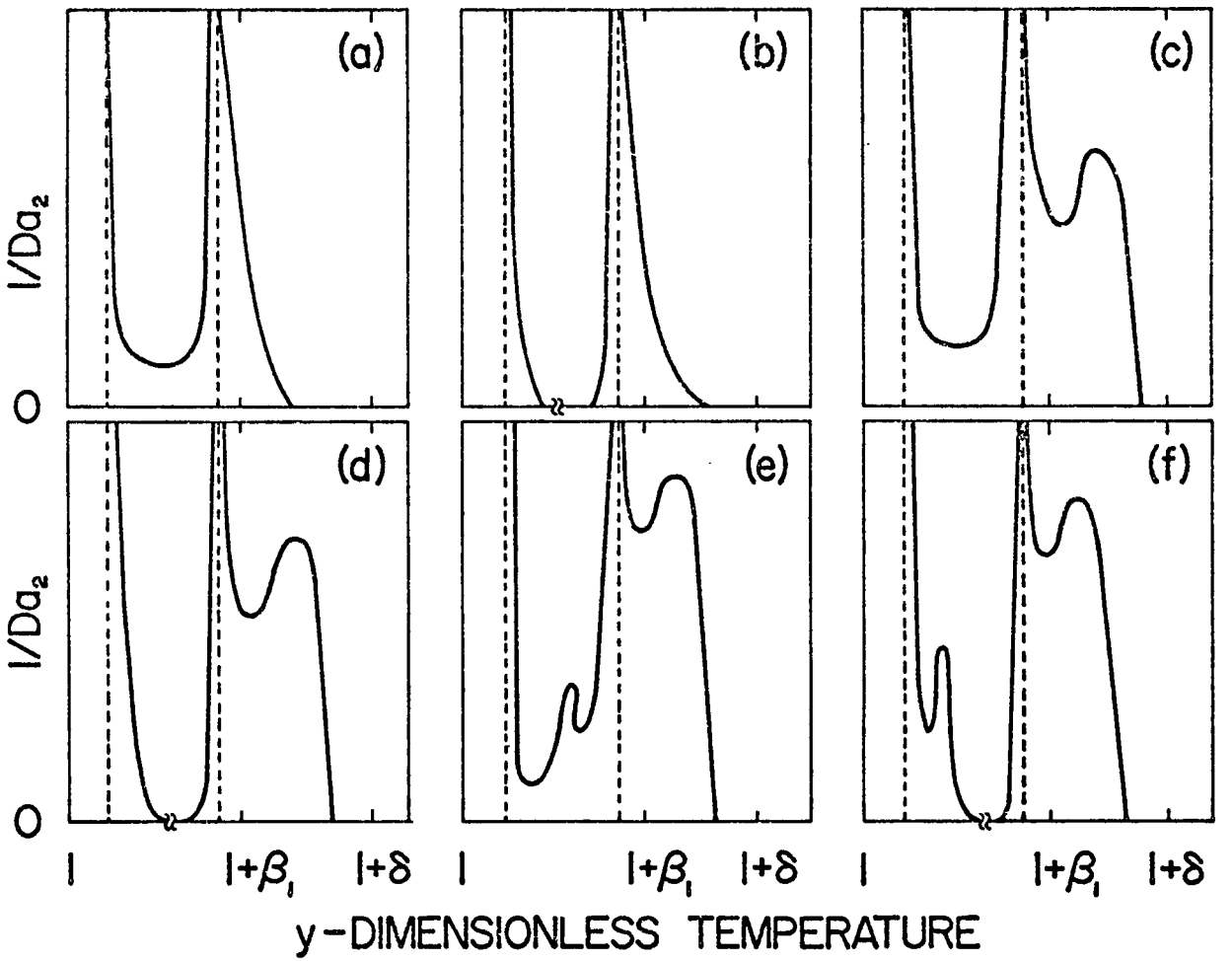


Figure 3: Various patterns of behavior for two exothermic reactions in the case of subproblems I and II.

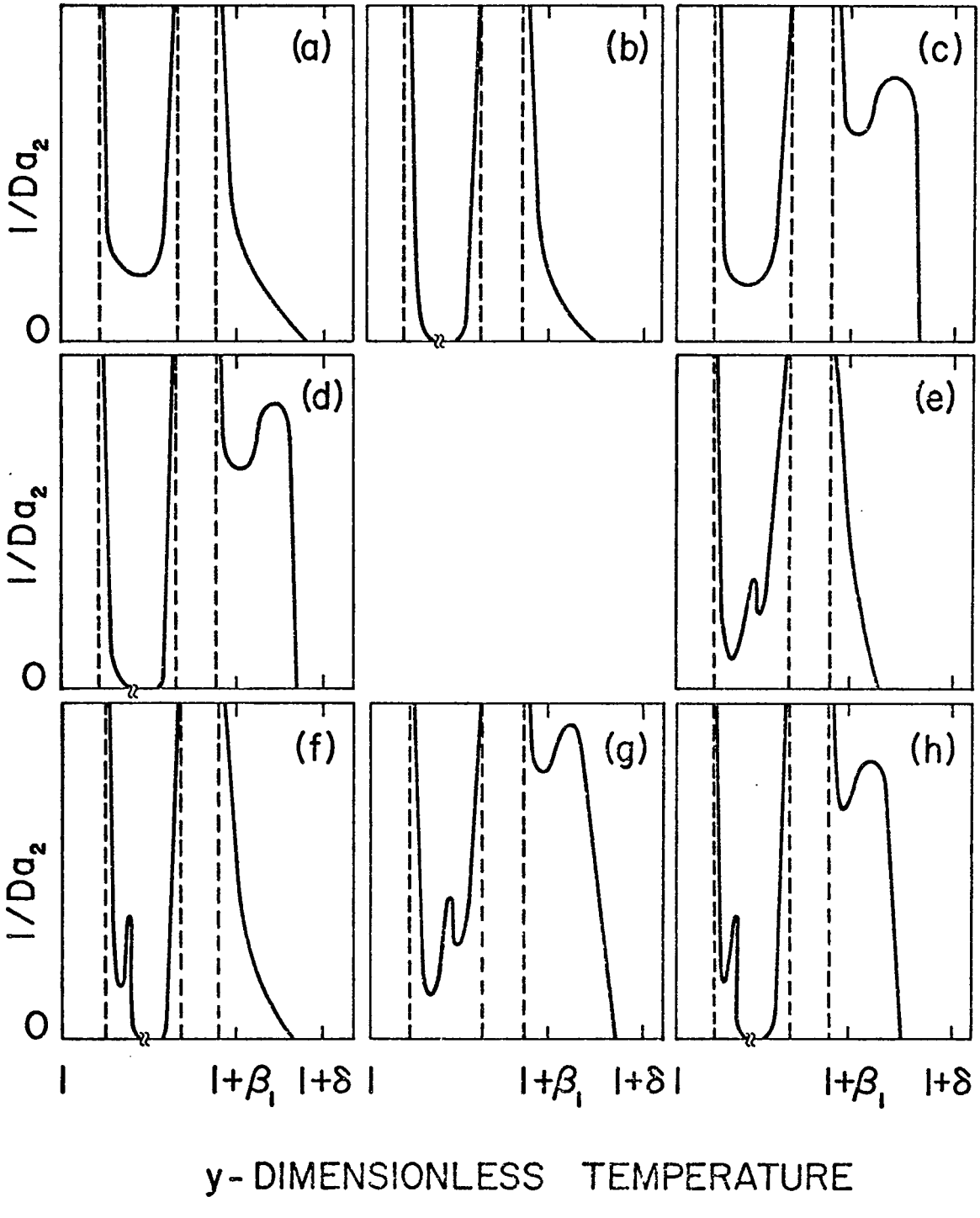


Figure 4: Various patterns of behavior for two exothermic reactions in the case of subproblems I and II.

$1/Da_2$ below which uniqueness is assured. For case (f), however, multiplicity as a function of Da_2 is of type 3-5-3 and occurs for all values of Da_2.

Figure 5 describes five possible patterns of (33) (with $\alpha=0$), when both reactions are exothermic. Observe that cases (a)-(e) are identical to those of figure 2.

Figure 6 describes four possible patterns of (21), when $\beta_1=0$, $\beta_2>0$. For case (a), uniqueness is assured for all values of Da_2. For cases (b) and (c), a maximum of three solutions could occur for some range of Da_2. For case (d), we find the surprising result of the occurence of a maximum of five steady state solutions for some range of Da_2 values (when $\beta_1>0$, $\beta_2=0$, no more than three solutions could occur).

Figures (7a)-(7k) describe eleven possible patterns of (42) for both subproblems I and II, when $\beta_1>0$. For cases (a), (b) and (f) uniqueness is assured for all values of $(-\beta_2)<0$. For cases (c), (d), (e), (g) and (h) a maximum of three solutions could occur for some range of $(-\beta_2)<0$. For cases (i), (j) and (k) a maximum of five steady state solutions could occur for some range of $(-\beta_2)<0$.

Figures (7l)-(7n) describe three possible patterns of $(-\beta_2)$ versus y (equ. 42) when $\beta_1=0$. For case (l), a unique steady state solution exists for all values of $(-\beta_2)<0$, while for case (m) a maximum of three solutions could occur

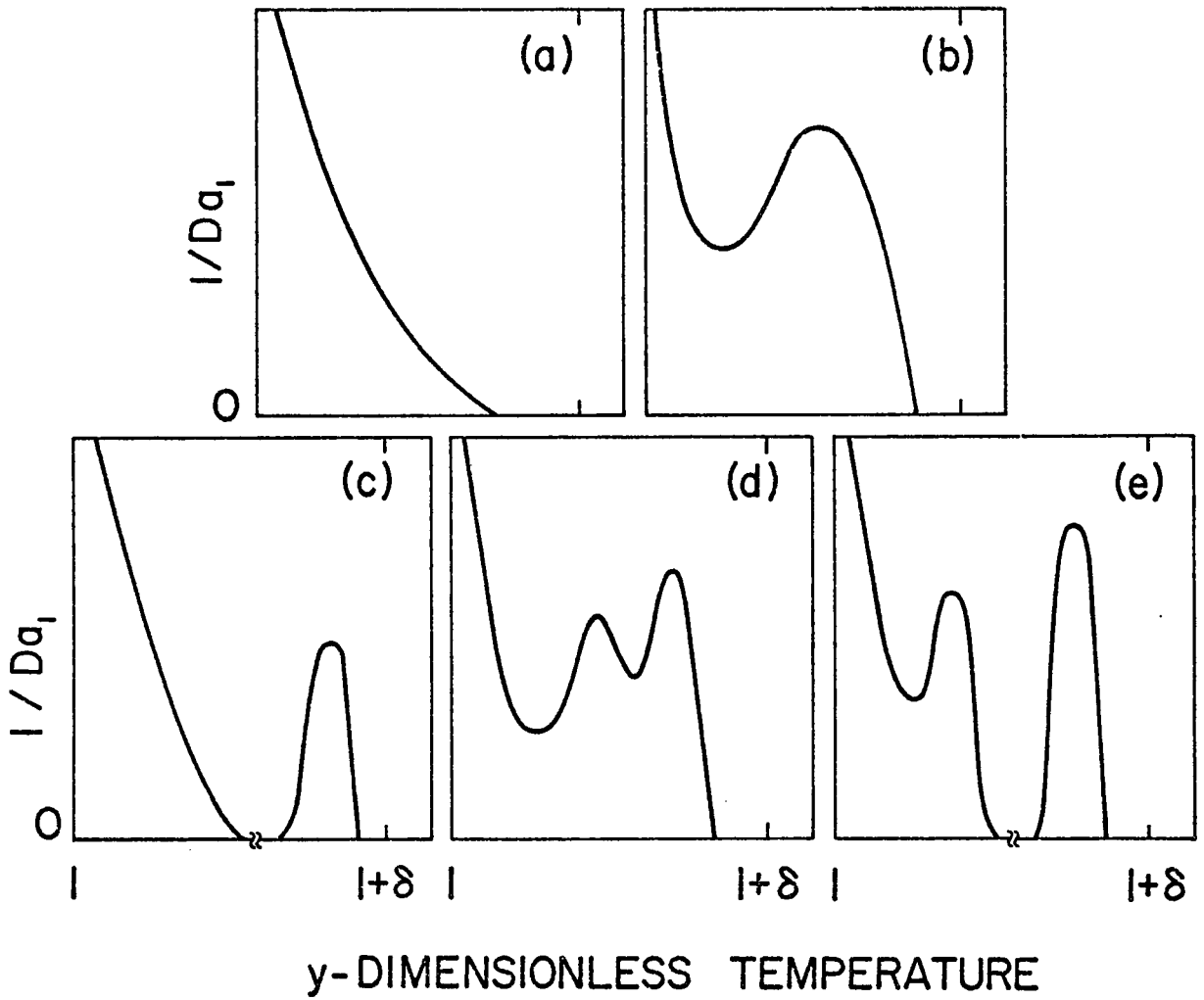


Figure 5: Various patterns of behavior for two exothermic reactions in the case of subproblem I(ii).

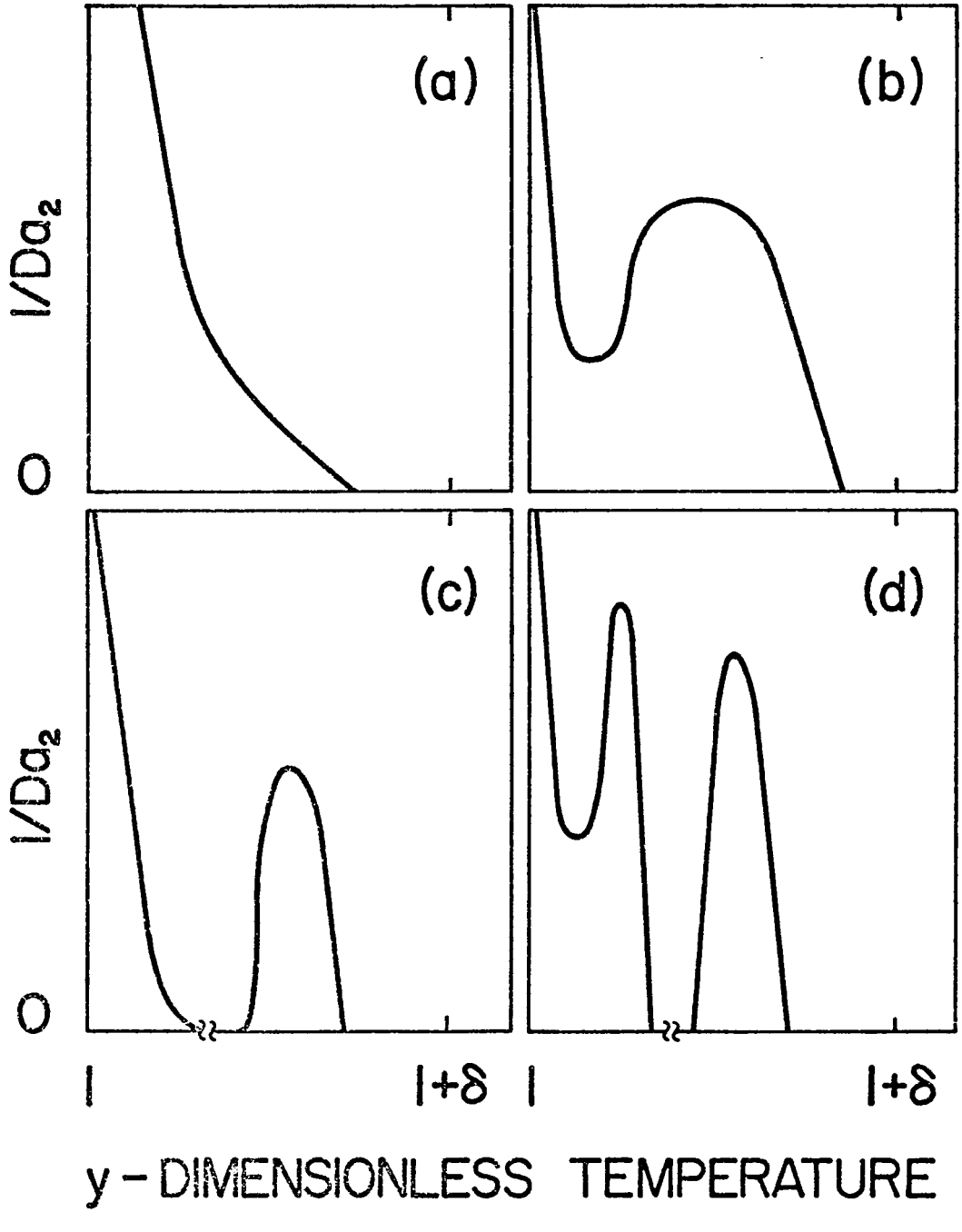


Figure 6: Various patterns of behavior when the first reaction is isothermal and the second is exothermic in the case of subproblem I.

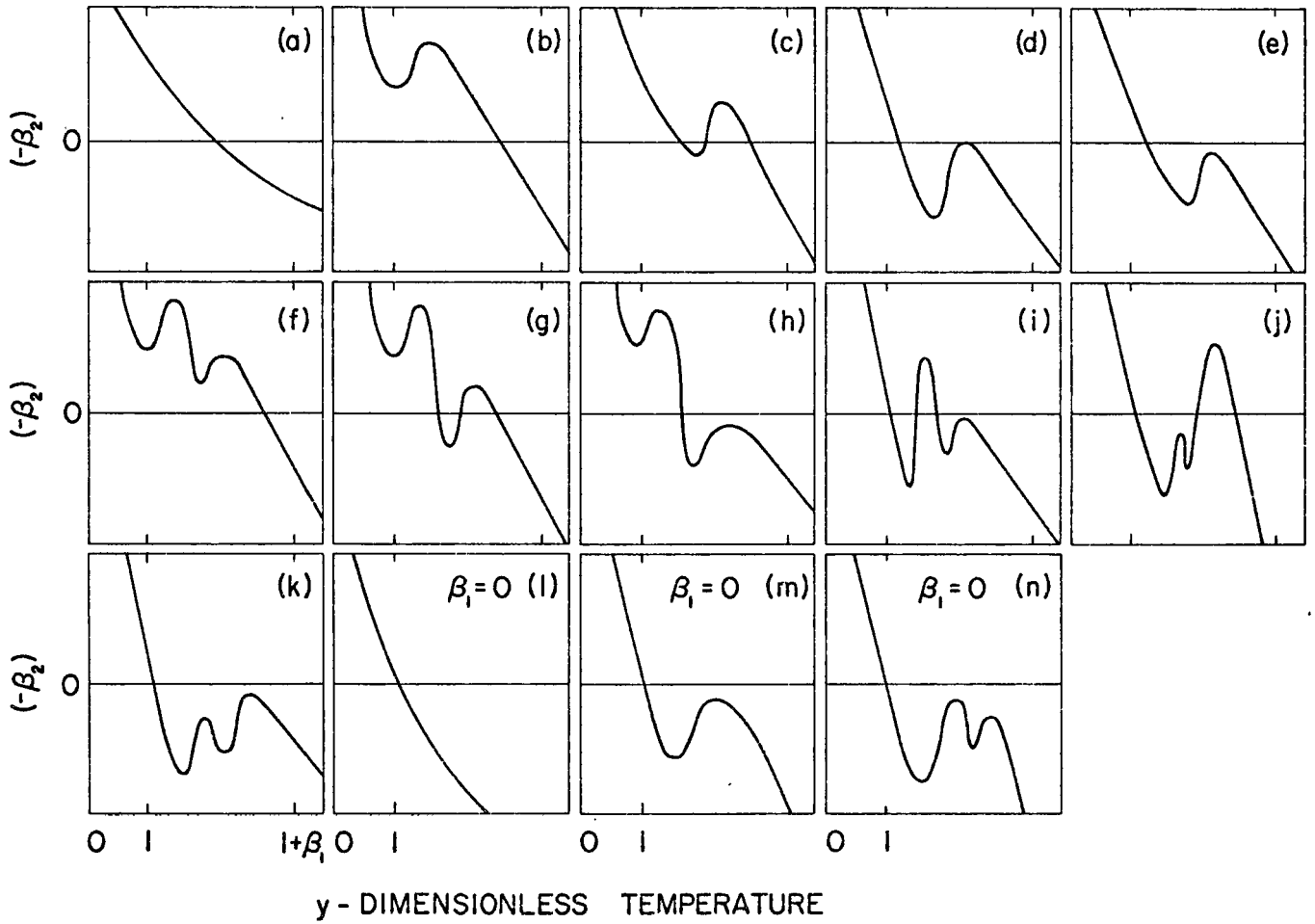


Figure 7: Typical behavior of the steady state equation (42) when the first reaction is either exothermic or isothermal in the case of subproblems I and II.

for some range of $(-\beta_2)<0$. For case (n), we have a maximum of five steady state solutions for some range of $(-\beta_2)<0$.

In figures (2)-(7), we denote

$$\delta \triangleq \beta_1+(\gamma+\alpha)\beta_2$$

and Appendix H gives parametric values for each figure.

Lemma 3B5: For $\beta_1>0, \beta_2>0$, the steady state equation (42) has multiple solutions for some values of $(-\beta_2)$, if equ. (19) has multiple roots. This also applies for the special case where $Da_1=Da_2$. Figures (7c), (7d), (7g), (7i) and (7j) illustrate cases where this Lemma certainly holds.

Lemma 3B6: A necessary and sufficient condition for uniqueness for all values of Da_1 of equ. (20) is

$$\gamma_1(\beta_1+\gamma\beta_2)<4(1+\alpha\beta_2)[1+\beta_1+(\gamma+\alpha)\beta_2] \tag{59}$$

Sufficient conditions for multiplicity for some values of Da_1 of equ. (20) are

$$\gamma_1(\beta_1+\gamma\beta_2)>4(1+\alpha\beta_2)[1+\beta_1+(\gamma+\alpha)\beta_2] \tag{60a}$$

$$\rho_1<y^* \tag{60b}$$

where y* is the largest root of equ. (20), and ρ_1 is the smallest root of the equation

$$(\beta_1+r\beta_2+\gamma_1)y^2-y\gamma_1\left\{\left[1+\beta_1+(r+\alpha)\beta_2\right]+(1+\alpha\beta_2)\right\}+\gamma_1(1+\alpha\beta_2)* \\ *\left[1+\beta_1+(r+\alpha)\beta_2\right]=0. \tag{60c}$$

The proof for Lemma 3B6 is shown in Appendix I. Lemma 3B6 can be used in Lemma 3B7.

Lemma 3B7: If (19) has one root only, then (21) has one asymptote, and a sufficient condition for multiplicity for some Da_2 values of (21) is that (20) has multiple roots (as in figures (2b) and (2e)). If, however, (20) has one root only (as in figures (2a), (2c) and (2d)), then it is still possible to derive sufficient conditions for multiplicity for some Da_2 values of (21) (Appendix J), except that they are rather impractical as they involve y*, which must be determined numerically.

Lemma 3B8: Suppose that (19) has multiple roots. Then, (21) will have either two (as in figure 3) or three asymptotes (as in figure 4), and multiplicity will occur for some Da_2 values of (21), if (20) has one root only (as in figures (3a), (3c), (3e), (4a), (4c), (4e) and (4g)). Our numerical calculations suggest that multiplicity will occur for ALL values of Da_2, if (20) has multiple roots (as in figures (3b), (3d), (3f), (4b), (4d), (4f) and

(4h)).

Our numerical calculations led us to the following important observation:

Consider (21) supposing that $\beta_1 > 0, \beta_2 > 0$.

If

(a) equ. (19) has multiple roots,

(b) equ. (20) has three roots not all of which occur in (y^{**}, $1+\delta$) [28], and

(c) F(y) has one hump in $(y^{**}, 1+\delta)$ where $1 < y^{**} < (1+\beta_1)$ is the largest root of (19),

THEN, (21) WILL DEFINATELY HAVE A MAXIMUM OF FIVE STEADY STATE SOLUTIONS FOR SOME RANGE OF Da_2 VALUES (as in figures (3d), (3f), (4d) and (4h)).

This Lemma allows us for the first time to derive sufficient conditions for the existence of FIVE steady state solutions for some values of Da_2, for both subproblems I and II when both reactions are exothermic.

Comment: We know that

$$(y-1) = \beta_1 \frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)} + \beta_1 \frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)} \qquad (61)$$

representing the steady state equation for a single first order chemical reaction occuring in a lumped parameter system has a maximum of three solutions. Surprisingly enough, the equation

$$(y-1)=\beta_1\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}+\beta_1\frac{\mathcal{D}a_2 X}{(1+\mathcal{D}a_2 X)},\ \sigma\neq 1 \tag{62}$$

has a maximum of five solutions for some Da_2 values of (21), when the following set of parametric values is used (see figure (4c)):

γ_1 =28.0

μ =1.0

$\beta_1=\beta_2$ =1.0

Da_1=0.0001

$\gamma\equiv$ 0.0

α =1.0

One may say that for this particular set of parametric values the condition

$$\frac{K_1(T_0)}{K_2(T_0)}\neq\frac{K_{ca}}{K_{cB}} \tag{63}$$

is necessary for the existence of a maximum of five solutions for some Da_2 values of (21). For subproblem I(i), however, we have found sets of parameter values for which a maximum of five solutions of (21) could occur for some Da_2 values even when (63) is violated.

For example (see figure (4f)),

γ_1 =25.0

μ =5.0

β_1 =0.875

β_2 =0.8

Da_1=0.0015

ν=0.00001

α =0.10

It should be noted that we have not been able to derive multiplicity criteria of any kind for the very special case where $Da_1=Da_2$ and $\beta_1=0, \beta_2>0$.

This concludes our analysis for subcase 3B.

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ADDENDUM

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On page 19 we derived sufficient conditions for uniqueness for all values of Da_1 in the case of subproblem I(ii). For subproblems I(i), II, sufficient conditions for uniqueness for all values of Da_1 have also been derived, and they are presented in Appendix R when $\beta_1 \geqslant 0, \beta_2>0$.

Subcase 3C: $B \triangleq \beta_2/\beta_1 < 0$

Introduction

This case is by far the most difficult to analyze. To the best of our knowledge, there are no results published in connection with uniqueness and multiplicity in the case of subproblems of I and II when one reaction is endothermic and the other is exothermic. Bilous and Amundson only made the remark [27] that for two first order chemical reactions $A \rightarrow B \rightarrow C$ occuring in a continuous stirred tank reactor a maximum of three steady state solutions could occur, and they presented two figures (but no parametric values) for illustration purposes for the case where one reaction is endothermic and the other is exothermic. However, uniqueness and multiplicity criteria were not derived in [27] either for subproblem I or subproblem II.

In order to acquire a feeling about the possible behavior of the system under investigation, extensive numerical calculations were performed using equ. (42). These numerical results have already been presented in figure 7 for $(-\beta_2) > 0$. We certainly agree with [27] that no more than three steady state solutions could occur for $\beta_1 > 0$, $\beta_2 < 0$. Our findings suggest that this is also true for subproblem II. From figure 7 we read that for cases (7a), (7d), (7e) and (7k) a unique steady state solution exists for all values of

$(-\beta_2)$ when $\beta_1>0, \beta_2<0$. For cases (7b), (7c), (7f), (7g), (7h), (7i) and (7j) a maximum of three steady state solutions could occur for some values of $(-\beta_2)$ when $\beta_1>0$, $\beta_2<0$. Actually, cases (7c), (7g), (7i) and (7j) led us to formulate the following Lemma for multiplicity:

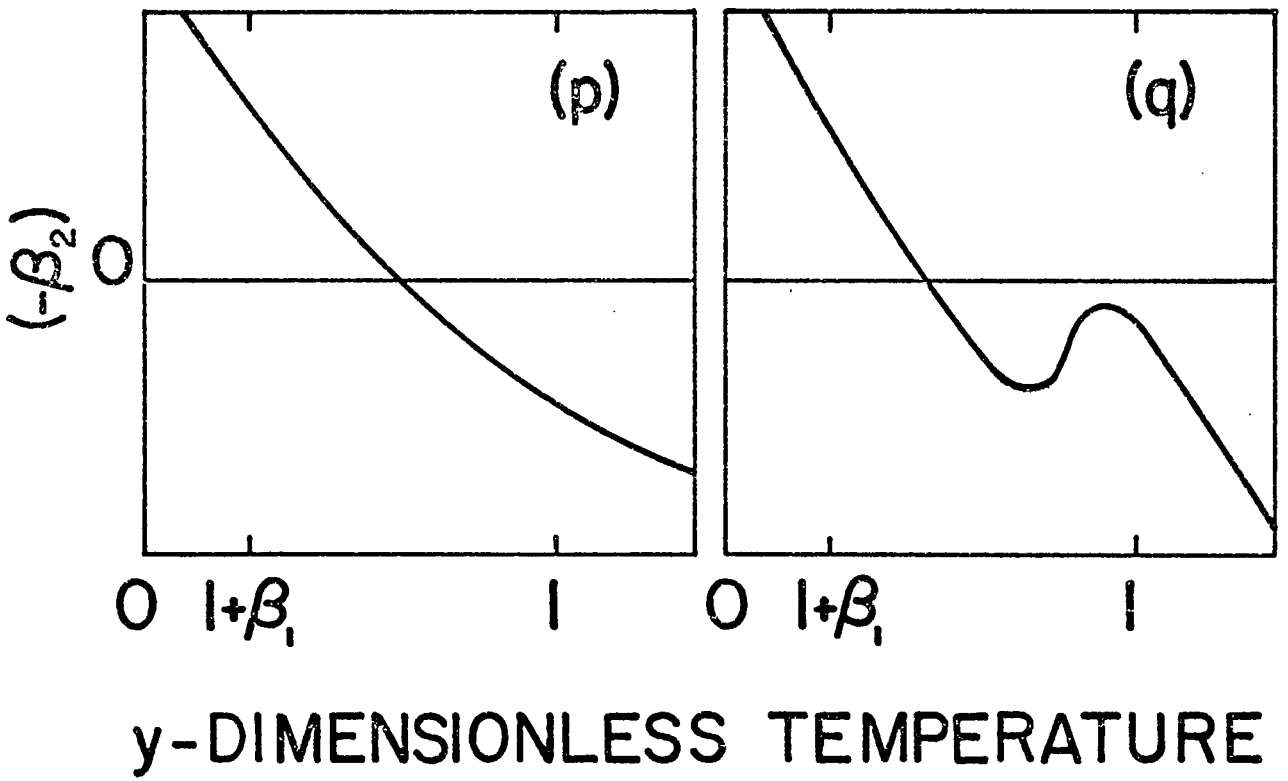
Lemma 3C1

Consider the steady state equation (42) supposing that $\beta_1>0, \beta_2<0$. A sufficient condition for multiplicity for some values of $(-\beta_2)>0$ is that equ. (19) has three roots in the interval $(1, 1+\beta_1)$.

Similarly, when $\beta_1<0$, $\beta_2>0$, figures (7p), (7q) demonstrate that a maximum of three steady state solutions could occur for some values of $(-\beta_2)<0$ of equ. (42). Observe that since $\beta_1<0$, equ. (19) has one root only.

Next, we need to derive sufficient conditions for uniqueness when $B \triangleq \beta_2/\beta_1<0$. The standard procedure has been to distinguish between the subcases $\beta_1>0, \beta_2<0$, and $\beta_1<0$, $\beta_2>0$, and derive uniqueness and multiplicity criteria for each subcase. However, this procedure cannot be used here because of certain difficulties encountered in working with the steady state equation (21) as shown below:

Suppose that $\beta_1>0, \beta_2<0$. Consider equ. (21). The



Figures (7p)-(7q): Typical behavior of the steady state equation (42) when the first reaction is endothermic in the case of subproblems I and II.

roots of the equation

$$[(y-1)-\mathcal{D}a_1 X(1+\beta_1-y)]=0$$

are in the interval (1, $1+\beta_1$), which means that the asymptotes of F(y) are in this interval. Consider equ. (20). Since $\beta_2<0$, it follows that $(1+\alpha\beta_2)<1<(1+\beta_1)$ and $[1+\beta_1+(\gamma+\alpha)\beta_2]<(1+\beta_1)$. There are two possibilities:

Either

$$(1+\alpha\beta_2)<1\leq[1+\beta_1+(\gamma+\alpha)\beta_2]<(1+\beta_1)$$

or

$$[1+\beta_1+(\gamma+\alpha)\beta_2]<1<(1+\beta_1)$$

In the latter case we have that either

$$(1+\alpha\beta_2)<[1+\beta_1+(\gamma+\alpha)\beta_2]<1<(1+\beta_1)$$

or

$$[1+\beta_1+(\gamma+\alpha)\beta_2]<(1+\alpha\beta_2)<1<(1+\beta_1)$$

When $(1+\alpha\beta_2)<1\leq[1+\beta_1+(\gamma+\alpha)\beta_2]<(1+\beta_1)$, we are facing the problem that even for the simple case where (19) and (20) have each a single root (say y**, y* respectively), we cannot predict whether y** $<$ y* or y** $>$ y*. In other words, it would be necessary to determine y** and y* numerically first to know whether F(y) has a positive or a negative slope as y $\longrightarrow$ y** for F(y) >0 , and THEN be able to write down sufficient conditions for uniqueness for all Da_2 of (21). Clearly, under these circumstances it would be preferable to plot F(y) rather than attempt to derive sufficient conditions for uniqueness. One may observe that the case

where

$$(1+\alpha\beta_2) < 1 \leq [1+\beta_1+(\gamma+\alpha)\beta_2] < (1+\beta_1)$$

could be handled much easier using the steady state equation (33) rather than (21), because we know that the roots of the denominator of $\Phi(y)$ (equ. (33)) are smaller than those of its numerator. This observation led us to the conclusion that to solve this difficult problem in a compact fashion, it would be necessary to use the steady state equations (21) and (33) interchangeably in deriving uniqueness and multiplicity criteria for $\beta_1 > 0$, $\beta_2 < 0$.

The same conclusion was reached when it became apparent that for $\beta_1 < 0$, $\beta_2 > 0$ similar difficulties occur when the steady state equation (21) is used, especially for

$$(1+\beta_1) < [1+\beta_1+(\gamma+\alpha)\beta_2] < 1 < (1+\alpha\beta_2).$$

Consequently, when $\beta_2/\beta_1 < 0$ and the intervals (1, $1+\beta_1$) and ($1+\alpha\beta_2$, $[1+\beta_1+(\gamma+\alpha)\beta_2]$) OVERLAP, then we are facing serious difficulties, because we cannot guess the sign of the slope of $F(y) > 0$ at $y \longrightarrow y^{**}$(asymptote).

After many attempts at presenting the results in a compact fashion, it became clear to us that it would be preferable to classify the problem in a different way depending on the sign of

$$[1+(\gamma+\alpha)B]$$

rather than the signs of β_1 and β_2 as was previously attempted. This type of classification makes the presentation

of the results both elegant and compact. The following two subcases will be distinguished:

Subcase I, $[1+(\gamma+\alpha)B] \leq 0$: Uniqueness and multiplicity criteria for this subcase will be derived using the steady state equation

$$\frac{1}{\mathcal{D}a_2} = \frac{X^{\mu}\left\{(1+\alpha\beta_2-y)+\mathcal{D}a_1 X[1+\beta_1+(\gamma+\alpha)\beta_2-y]\right\}}{[(y-1)-\mathcal{D}a_1 X(1+\beta_1-y)]} \triangleq F(y) \tag{64}$$

because (64) allows for compactness in the presentation of the results.

Subcase II, $[1+(\gamma+\alpha)B] > 0$: Uniqueness and multiplicity criteria for this subcase will be derived using the steady state equation

$$\frac{1}{\mathcal{D}a_1} = \frac{X\left\{(1+\beta_1-y)+\mathcal{D}a_2 X^{\mu}[1+\beta_1+(\gamma+\alpha)\beta_2-y]\right\}}{[(y-1)-\mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2-y)]} \triangleq \Phi(y) \tag{65}$$

rather than equ. (64), because (65) allows for compactness in the presentation of the results also.

We are certainly aware that the criteria derived for subcase II are different from those of subcase I: In subcase I, uniqueness criteria are derived for all values of Da_2, while in subcase II they derived for all values of Da_1.

SUBCASE I: $[1+(\gamma+\alpha)B] \leq 0$

Uniqueness and multiplicity criteria will be derived using the steady state equation (64) when $B \triangleq \beta_2/\beta_1 < 0$ for both subproblems I and II (see CHAPTER II). Figures will be presented first to acquire a feeling about the possible behavior of the system when $[1+(\gamma+\alpha)B] \leq 0$.

The results of extensive numerical calculations are presented in figure 8, which describes nine possible patterns of (64) when $B \triangleq \beta_2/\beta_1 < 0$ and $[1+(\gamma+\alpha)B] \leq 0$ for each of subproblems I and II.

Figures (8a)-(8c) describe the possible behavior of (64) when $\beta_1 < 0$, $\beta_2 > 0$, and $[1+(\gamma+\alpha)B] \leq 0$. For case (8a), a unique steady state solution exists for all Da_2 of (64). For cases (8b) and (8c), a maximum of three solutions could occur for some range of Da_2 values. Since $\beta_1 < 0$, F(y) has one asymptote only in the case of figures (8a)-(8c).

Figures (8d)-(8i) describe the possible behavior of (64) when $\beta_1 > 0$, $\beta_2 < 0$, and $[1+(\gamma+\alpha)B] \leq 0$. For cases (8d)-(8g), F(y) has one asymptote only, while for cases (8h)-(8i) F(y) has three asymptotes. A unique steady state solution exists for all Da_2 of (64) in cases (8d)-(8e), while for cases (8f)-(8g) a maximum of three solutions could occur for some range of Da_2. For cases (8h)-(8i), multiplicity as a function of Da_2 is of type 3-1, and there is an upper bound

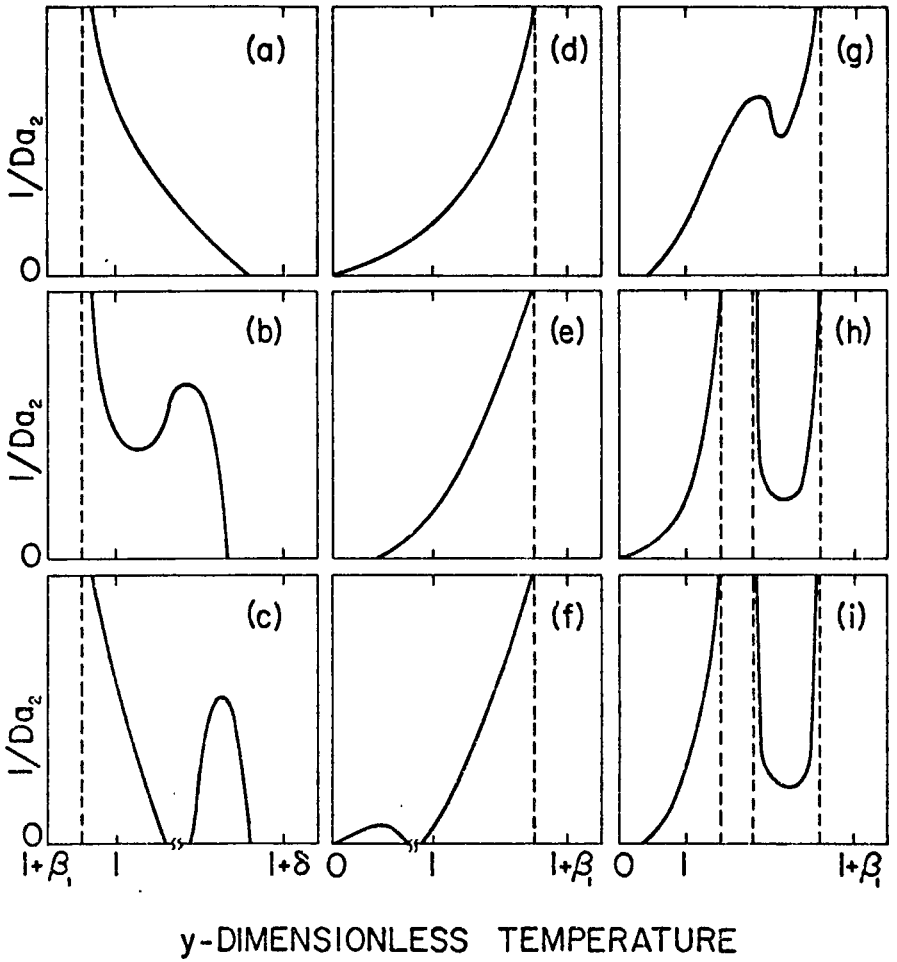


Figure 8: Various patterns of behavior when one reaction is endothermic and the other is exothermic in the case of subproblems I and II.

on $1/Da_2$ below which uniqueness is assured.

Our numerical calculations suggest that no more than three steady state solutions could occur when $B < 0$ and $[1+(\gamma+\alpha)B] \leq 0$, eventhough this result has not been proved analytically. Parametric values for figures (8a)-(8i) are presented in Appendix K.

1. Multiplicity criteria for subcase I

From figure 8, we are able to formulate the following Lemmas concerning steady state multiplicity:

Lemma 3C2: Consider (64) supposing that $\beta_1 < 0$, $\beta_2 > 0$. A sufficient condition for multiplicity for some Da_2 values of (64) is that the equation (20)

$$(1+\alpha\beta_2-y)+\mathcal{D}a_1 X[1+\beta_1+(\gamma+\alpha)\beta_2-y]=0 \qquad (20)$$

has multiple roots (as in figure (8c)).

If, however, (20) does not have multiple roots (see Appendix L, figure (8b)), then it is still possible to derive sufficient conditions for multiplicity for some Da_2 of (64), except that they rather impractical because they involve y_1 (the largest root of (20)), which must be determined numerically.

Lemma 3C3: Consider (64) supposing that $\beta_1 > 0$, $\beta_2 < 0$. If equ. (19)

$$[(y-1) - \mathcal{D}a_1 X (1+\beta_1 - y)] = 0 \qquad (19)$$

has only one root, then F(y) (as defined by (64)) will have only one asymptote (as in figures (8d)-(8g)), and a sufficient condition for multiplicity for some Da_2 values is that equ. (20) has multiple roots (as in figure (8f)).

If, however, (20) does not have multiple roots, then it is still possible to derive multiplicity criteria for some Da_2 values, except that they are rather impractical since they involve y* (the largest root of (20)), which must be determined numerically (see figure (8g)).

If equ. (19) has multiple roots, then F(y) will have more than one asymptote (as in figures (8h)-(8i)), and multiplicity will occur for some Da_2 values if equ. (20) has only one root.

2. Uniqueness criteria for subcase I

From figures (8a) and (8d)-(8e) we are able to formulate the following Lemma concerning uniqueness:

Lemma 3C4: Let's rewrite the steady state equation (64) in the form

$F(y) = F_N / F_D$

and suppose that Da_1 is such that the equation

$$\left[(y-1)-\mathcal{D}a_1 \mathbb{X}(1+\beta_1-y)\right]=0 \tag{66}$$

has only one root, y**, so that F(y) has one asymptote, and let y_1 denote the largest root of the equation

$$(1+\alpha\beta_2-y)+\mathcal{D}a_1 \mathbb{X}\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]=0 \tag{67}$$

Then, a necessary and sufficient condition for uniqueness for all Da_2 of (64) is

$$F'(y)=\begin{cases} <0\,,\ \beta_1<0,\beta_2>0\,,(1+\beta_1)<y^{**}<y<y_\ell<\max[1+\alpha\beta_2,1+\delta] & \text{(68a)} \\ >0\,,\ \beta_1>0,\beta_2<0\,,\ y^{+}<y<y^{**}<(1+\beta_1) & \text{(68b)} \end{cases}$$

where y^{+} is defined in Appendix M.

Conditions (68a)-(68b) yield the following sufficient conditions for uniqueness for all Da_2 of equ. (64):

---

1. $[1+(\gamma+\alpha)B]<0$

(a) Subproblem I(i): ($\gamma \neq 0$, $\alpha \neq 0$)

When $\beta_1 > 0, \beta_2 < 0$, require that either

$$(2\beta_1 + \gamma\beta_2) > 0 \quad \text{.....(68c)}$$

$$(\alpha\beta_2 + \mu\gamma_1) < 0 \quad \text{.....(68d)}$$

$$\mu\gamma_1[2(1+\beta_1)+(\gamma+\alpha)\beta_2]^2 < 4(\mu\gamma_1+\alpha\beta_2)\left[1+\alpha\beta_2+(2\beta_1+\gamma\beta_2)(1+\beta_1)-\frac{\gamma\beta_1\beta_2}{4\mu}+\alpha\beta_1\overline{M}\right] \quad (68e)$$

or

$$(2\beta_1+\gamma\beta_2) \leq 0 \quad \text{.....(68f)}$$

$$(\alpha\beta_2+\mu\gamma_1) < 0 \quad \text{.....(68g)}$$

$$\mu\gamma_1(\alpha\beta_2+2)^2 < 4(\alpha\beta_2+\mu\gamma_1)\left\{1+\alpha\beta_2(1+\beta_1)-\beta_1\left[\alpha\beta_2+2\beta_1+\gamma\beta_2\left(1+\frac{1}{4\mu}\right)\right]+ +\alpha\beta_1\overline{M}\right\} \quad (68h)$$

where $\overline{M}$ is given by (79e) in the next section containing the proofs.

When $\beta_1 < 0$, $\beta_2 > 0$, require that either

$$(2\beta_1+\gamma\beta_2) \geqslant 0 \quad \text{.....(68i)}$$

$$\mu\gamma_1(\alpha\eta_1+2)^2 < 4(\alpha\beta_2+\mu\gamma_1)\left[1+\alpha\eta_1(1+\beta_1)-\alpha\beta_1\beta_2+\beta_1\overline{M}^*\right] \quad (68j)$$

or

$$(2\beta_1+\gamma\beta_2)<0 \qquad \text{(68k)}$$

$$\mu\gamma_1\left[2+\beta_2\left(\alpha+\frac{\gamma}{4\mu}\right)\right]^2<4(\mu\gamma_1+\alpha\beta_2)\left[1+\beta_2(1+\beta_1)\left(\alpha+\frac{\gamma}{4\mu}\right)-\right.$$
$$\left.-\beta_1\left[2\beta_1+(\gamma+\alpha)\beta_2\right]+\beta_1\overline{M}^*\right] \qquad \text{(68L)}$$

where $\overline{M}^*$ is given by (82c) and η_1 by (84c) in the next section containing the proofs.

(b) Subproblem I(ii): ($\gamma\neq 0$, $\alpha=0$)

When $B\triangleq\beta_2/\beta_1<0$ and $[1+(\gamma+\alpha)B]<0$, sufficient conditions for uniqueness for all Da_2 of (64) have been derived, but they are impractical because knowledge of y**, y is required which must be determined numerically. Derivation of these conditions is shown in the next section containing the proofs.

(c) Subproblem II: ($\gamma\equiv 0$, $\alpha\neq 0$)

When $B\triangleq\beta_2/\beta_1<0$ and $[1+(\gamma+\alpha)B]<0$, sufficient conditions for uniqueness for all Da_2 of (64) are given by (91a)-(93) in the next section containing the proofs.

2. $[1+(\gamma+\alpha)B]=0$

(a) Subproblem I(i): ($\gamma\neq 0$, $\alpha\neq 0$)

When $\beta_1<0$, $\beta_2>0$, it suffices for uniqueness for all Da_2 of (64) that

$$\mu\gamma_1\left[2+\beta_2\left(\alpha+\frac{\gamma}{4\mu}\right)\right]^2<4\left(\mu\gamma_1+\alpha\beta_2\right)*$$
$$*\left[1+\left(\alpha+\frac{\gamma}{4\mu}\right)\beta_2(1+\beta_1)-\beta_1^2+\beta_1\overline{M}^*\right] \tag{68m}$$

where M* is given by (82c) with $[\beta_1+(\gamma+\alpha)\beta_2]=0$ in the next section containing the proofs.

(b) Subproblem I(ii): ($\gamma\neq 0$, $\alpha=0$)

When $\beta_1>0$, $\beta_2<0$, it suffices for uniqueness for all Da_2 of (64) that

$$\left[\mu\gamma_1+\frac{\gamma\beta_2\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]<0 \tag{68n}$$

$$\mu\gamma_1\left[2+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}+\frac{\gamma\beta_2}{4\mu}\right]^2<4\left[\mu\gamma_1+\frac{\gamma\beta_2\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]*$$
$$*\left[1+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}+\frac{\gamma\beta_2}{4\mu}\right] \tag{68o}$$

When $\beta_1<0$, $\beta_2>0$, it suffices for uniqueness for all Da_2 of (64) that

$$\mu\gamma_1\left[2+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}\right]^2<4\left[\mu\gamma_1+\frac{\gamma\beta_2\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]\left[1+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}\right] \tag{68p}$$

The proofs for these criteria are shown in the next section.

(c) Subproblem II: ($\gamma \equiv 0$, $\alpha \neq 0$)

When $\beta_1 < 0$, $\beta_2 > 0$, it suffices for uniqueness for all Da_2 of (64) that

$$\mu\gamma_1(2+\alpha\beta_2)^2 < 4(\mu\gamma_1+\alpha\beta_2)\left[1+\alpha\beta_2(1+\beta_1)-\beta_1^2+\beta_1\overline{M}^*\right] \tag{68q}$$

where $\overline{M}^*$ is given by (82c) with $[\beta_1+(\gamma+\alpha)\beta_2]=0$. Derivation of this criterion follows directly from the one for subproblem I(i) shown above.

This concludes Lemma 3C4 on uniqueness.

The next section contains proofs for all the conditions shown above which follow from Lemma 3C4.

PROOFS OF THE UNIQUENESS CRITERIA FOR SUBCASE I: $[1+(\gamma+\alpha)B] \leq 0$

PROOF

FOR SUBPROBLEM I(i)

WHEN $[1+(\nu+\alpha)B]<0$ AND $B<0$

Conditions (68a)-(68b) can be rewritten as

$$\beta_2 y^2+\mu\gamma_1(y-1)\Theta(y)\left\{y-1-\alpha\beta_2-\left[h_1(y)+h_2(y)\right]\right\}+$$

$$+\mu\gamma_1\beta_1 M(y)=\begin{cases}<0\,, & \beta_1>0,\beta_2<0,y^{+}<y<y^{**} \quad (69a)\\ >0\,, & \beta_1<0,\beta_2>0,y^{**}<y<y_{\ell} \quad (69b)\end{cases}$$

where

$$\Theta(y)\triangleq\frac{1}{\left[\alpha+\dfrac{\nu\mathcal{D}a_1\mathbb{X}}{(1+\mathcal{D}a_1\mathbb{X})}\right]}>0 \qquad (70a)$$

$$h_1(y)\triangleq\frac{(2\beta_1+\nu\beta_2)}{\left(1+\dfrac{1}{\mathcal{D}a_1\mathbb{X}}\right)} \qquad (70b)$$

$$h_2(y)\triangleq\frac{\nu\beta_2\mathcal{D}a_1\mathbb{X}}{\mu(1+\mathcal{D}a_1\mathbb{X})^2}=\begin{Bmatrix}<0\,, & \beta_1>0,\beta_2<0\\ >0\,, & \beta_1<0,\beta_2>0\end{Bmatrix} \qquad (70c)$$

$$M(y) \triangleq \frac{\mu \mathcal{D}a_1^2 X^2 [\beta_1 + (\gamma+\alpha)\beta_2] + (\mu-1)\alpha\beta_2 \mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)[\alpha(1+\mathcal{D}a_1 X) + \gamma \mathcal{D}a_1 X]} \tag{70d}$$

Since the sign of (y-1) is not known, we prefer to rewrite (69a)-(69b) as

$$\beta_2 y^2 + \mu\gamma_1 \theta(y)(y-1)^2 - \mu\gamma_1 \theta(y)(y-1-\beta_1+\beta_1)[\alpha\beta_2 + h_1(y) + h_2(y)] +$$

$$+\mu\gamma_1\beta_1 M(y) = \begin{cases} <0\,, \beta_1>0, \beta_2<0\,, y^{+}<y<y^{**} & \text{(71a)} \\ >0\,, \beta_1<0, \beta_2>0\,, y^{**}<y<y_{\ell} & \text{(71b)} \end{cases}$$

For (71a) to hold it suffices that

$$\beta_2 y^2 + \mu\gamma_1 (y-1)^2 \bar{\theta} + \mu\gamma_1 \bar{\theta}(1+\beta_1-y)(\alpha\beta_2 + \bar{h}_1) -$$

$$-\mu\gamma_1\beta_1(\alpha\beta_2 + \underline{h_1} + \underline{h_2})\bar{\theta} + \mu\gamma_1\beta_1 \bar{M} < 0 \tag{72}$$

where y $\in$ (y, y**)

while for (71b) to hold it suffices that

$$\beta_2 y^2+\mu\gamma_1\bar{\theta}(y-1)^2-\mu\gamma_1(y-1-\beta_1)(\alpha\beta_2+\bar{h}_1+\bar{h}_2)\bar{\theta}-$$
$$-\mu\gamma_1\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)\bar{\theta}+\mu\gamma_1\beta_1\bar{\theta}\,\overline{M}^*>0 \qquad (73)$$

where y $\in$ (y**, y_1) and

$$M^*(y)\triangleq M(y)/\theta(y) \qquad (73a)$$

Conditions (72)-(73) can be rewritten respectively as

$$y^2(\beta_2+\mu\gamma_1\bar{\theta})-y\mu\gamma_1(2+\alpha\beta_2+\bar{h}_1)\bar{\theta}+$$
$$+\mu\gamma_1\left[\bar{\theta}+(1+\beta_1)(\alpha\beta_2+\bar{h}_1)\bar{\theta}-\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)\bar{\theta}+\beta_1\overline{M}\right]<0 \qquad (74)$$

where y $\in$ (y^+, y**) and

$$y^2(\beta_2+\mu\gamma_1\bar{\theta})-y\mu\gamma_1(2+\alpha\beta_2+\bar{h}_1+\bar{h}_2)\bar{\theta}+$$
$$+\mu\gamma_1\bar{\theta}\left[1+(1+\beta_1)(\alpha\beta_2+\bar{h}_1+\bar{h}_2)-\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)+\beta_1\overline{M}^*\right]>0 \qquad (75)$$

where y $\in$ (y**, y_1)

For (74) to hold, it suffices that either

$$(\beta_2+\mu\gamma_1\bar{\theta})<0 \quad \text{.....(76a)}$$

$$\mu\gamma_1\bar{\theta}^2(2+\alpha\beta_2+\bar{h}_1)^2<4(\beta_2+\mu\gamma_1\bar{\theta})*$$
$$*\left\{\bar{\theta}\left[1+(1+\beta_1)(\alpha\beta_2+\bar{h}_1)-\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)\right]+\beta_1\bar{M}\right\} \quad (76b)$$

or

$$(\beta_2+\mu\gamma_1\bar{\theta})>0 \quad \text{.....(77a)}$$

$$\mu\gamma_1\bar{\theta}^2(2+\alpha\beta_2+\bar{h}_1)^2>4(\beta_2+\mu\gamma_1\bar{\theta})*$$
$$*\left\{\bar{\theta}\left[1+(1+\beta_1)(\alpha\beta_2+\bar{h}_1)-\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)\right]+\beta_1\bar{M}\right\}$$

(77b)

$$\rho_1<y^+<y^{**}<\rho_2 \quad \text{.....(77c)}$$

where ρ_1 , ρ_2 are roots of the equation (74)=0. Conditions (77a)-(77c) are rather impractical since they involve y, y** which must be determined numerically.

For (75) to hold it suffices that

$$\mu\gamma_1\bar{\theta}(2+\alpha\beta_2+\bar{h}_1+\bar{h}_2)^2<4(\beta_2+\mu\gamma_1\bar{\theta})*$$
$$*\left[1+(1+\beta_1)(\alpha\beta_2+\bar{h}_1+\bar{h}_2)-\beta_1(\alpha\beta_2+\underline{h}_1+\underline{h}_2)+\beta_1\bar{M}^*\right]$$

(78)

Consequently, (69a) will hold if either (76a)-(76b) or (77a)-(77c) hold, while (69b) will hold if (78) holds.

When $\beta_1 > 0$, $\beta_2 < 0$, the following substitutions are made:

$$\bar{\theta} = 1/\alpha \quad , \quad \underline{\theta} = \theta(1+\beta_1) \quad \ldots\ldots\ldots\ldots \quad (79a)$$

$$\bar{h}_2 = 0 \quad , \quad \underline{h_2} = \gamma\beta_2/4\mu \quad \ldots\ldots\ldots\ldots \quad (79b)$$

$$\bar{h}_1 = \begin{cases} (2\beta_1 + \gamma\beta_2) & \text{if } (2\beta_1 + \gamma\beta_2) > 0 \\ 0 & \text{if } (2\beta_1 + \gamma\beta_2) \leq 0 \end{cases} \quad (79c)$$

$$\underline{h_1} = \begin{cases} 0 & \text{if } (2\beta_1 + \gamma\beta_2) \geq 0 \\ (2\beta_1 + \gamma\beta_2) & \text{if } (2\beta_1 + \gamma\beta_2) < 0 \end{cases} \quad (79d)$$

$$\bar{M} = \begin{cases} 0 & \text{if } \mu \geq 1 \\ \dfrac{(\mu-1)\alpha\beta_2}{\mu(\gamma+2\alpha)} & \text{if } \mu < 1 \end{cases} \quad (79e)$$

(see Appendix N)

Thus, (76a)-(76b) will hold if either

$$(2\beta_1 + \gamma\beta_2) > 0 \quad \cdots\cdots \quad (80a)$$

$$(\alpha\beta_2 + \mu\gamma_1) < 0 \quad \cdots\cdots \quad (80b)$$

$$\mu\gamma_1\left[2(1+\beta_1)+(\gamma+\alpha)\beta_2\right]^2 < 4(\mu\gamma_1+\alpha\beta_2) *$$

$$* \left[1+\alpha\beta_2+(2\beta_1+\gamma\beta_2)(1+\beta_1)-\frac{\gamma\beta_1\beta_2}{4\mu}+\alpha\beta_1\overline{M}\right] \quad (80c)$$

or

$$(2\beta_1 + \gamma\beta_2) \leq 0 \quad \cdots\cdots \quad (81a)$$

$$(\alpha\beta_2 + \mu\gamma_1) < 0 \quad \cdots\cdots \quad (81b)$$

$$\mu\gamma_1\left(\beta_2+\frac{2}{\alpha}\right)^2 < 4\left(\beta_2+\frac{\mu\gamma_1}{\alpha}\right) *$$

$$* \left\{\frac{1}{\alpha}+\beta_2(1+\beta_1)-\frac{\beta_1}{\alpha}\left[\alpha\beta_2+2\beta_1+\gamma\beta_2\left(1+\frac{1}{4\mu}\right)\right]+\beta_1\overline{M}\right\} \quad (81c)$$

When $\beta_1 < 0$, $\beta_2 > 0$, the following substitutions are made:

$$\underline{\theta} = \theta\left(\sup[1+\alpha\beta_2, 1+\delta]\right), \quad \bar{\theta} = 1/\alpha \tag{82a}$$

$$\underline{h_2} = 0 \quad , \quad \bar{h}_2 = \gamma\beta_2/4\mu \tag{82b}$$

$$\bar{M}^* = \begin{cases} [\beta_1 + (\gamma+\alpha)\beta_2] + \dfrac{(\mu-1)\alpha\beta_2}{2\mu} & \text{if } \mu \geqslant 1 \\ [\beta_1 + (\gamma+\alpha)\beta_2] & \text{if } \mu < 1 \end{cases} \tag{82c}$$

(see Appendix N)

$\bar{h}_1$ and $\underline{h}_1$ are given by (79c)-(79d) respectively.

Thus, (78) will hold if either

$$(2\beta_1 + \gamma\beta_2) \geqslant 0 \tag{83a}$$

$$\mu\gamma_1\left(\eta_1 + \frac{2}{\alpha}\right)^2 < 4\left(\beta_2 + \frac{\mu\gamma_1}{\alpha}\right)\left[\frac{1}{\alpha} + \eta_1(1+\beta_1) - \beta_1\beta_2 + \frac{\beta_1\bar{M}^*}{\alpha}\right] \tag{83b}$$

or

$$(2\beta_1+\nu\beta_2)<0 \qquad (84a)$$

$$\mu\gamma_1\left[2+\left(\alpha+\frac{\nu}{4\mu}\right)\beta_2\right]^2<4(\mu\gamma_1+\alpha\beta_2)*$$

$$*\left[1+\beta_2(1+\beta_1)\left(\alpha+\frac{\nu}{4\mu}\right)-\beta_1\left[2\beta_1+(\nu+\alpha)\beta_2\right]+\beta_1\overline{M}^*\right] \qquad (84b)$$

where

$$\eta_1 \triangleq \frac{1}{\alpha}\left[\alpha\beta_2+2\beta_1+\nu\beta_2\left(1+\frac{1}{4\mu}\right)\right] \qquad (84c)$$

and $\bar{M}^*$ is given by (82c).

Therefore, either (80a)-(80c) or (81a)-(81c) are sufficient conditions for uniqueness for all Da_2 of (64) when $\beta_1>0$, $\beta_2<0$, while (83a)-(83b) or (84a)-(84b) are sufficient conditions for uniqueness for all Da_2 of (64) when $\beta_1<0$, $\beta_2>0$. These uniqueness criteria apply for subproblem I(i) when $B\triangleq\beta_2/\beta_1<0$ and $[1+(\nu+\alpha)B]<0$.

PROOF

FOR SUBPROBLEM I(ii)

WHEN $[1+(\gamma+\alpha)B]<0$ AND $B<0$

For subproblem I(ii) (α =0), we have that

$$\Theta(y) \triangleq \frac{(1+\mathcal{D}a_1 X)}{\gamma \mathcal{D}a_1 X} > 0 \tag{85a}$$

$$M(y) \triangleq \frac{(\beta_1+\gamma\beta_2)/\gamma}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)} = \begin{cases} <0 \ , \ \beta_1>0, \beta_2<0 \\ >0 \ , \beta_1<0, \beta_2>0 \end{cases} \tag{85b}$$

$h_1(y)$ and $h_2(y)$ are given by (70b)-(70c) respectively.

When $\beta_1>0$, $\beta_2<0$, it suffices for uniqueness for all Da_2 values of (64) that either

$$(2\beta_1+\gamma\beta_2)>0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{86a}$$

$$(\beta_2+\mu\gamma_1\bar{\Theta})<0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{86b}$$

$$\mu\gamma_1\bar{\Theta}^2[2(1+\beta_1)+\gamma\beta_2]^2<4(\beta_2+\mu\gamma_1\bar{\Theta})* \\ *\left\{\bar{\Theta}\left[1+(1+\beta_1)(2\beta_1+\gamma\beta_2)-\frac{\gamma\beta_1\beta_2}{4\mu}\right]+\beta_1\bar{M}\right\} \tag{86c}$$

or

$$(2\beta_1+\gamma\beta_2)\leq 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{87a}$$

$$(\beta_2+\mu\gamma_1\bar{\Theta})<0 \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{87b}$$

$$\mu\gamma_1\bar{\theta}^2 < (\beta_2+\mu\gamma_1\bar{\theta})\left\{\bar{\theta}\left[1-\beta_1\left(2\beta_1+\nu\beta_2\left(1+\frac{1}{4\mu}\right)\right)\right]+\beta_1\bar{M}\right\} \tag{87c}$$

When $\beta_1 < 0$, $\beta_2 > 0$, it suffices for uniqueness for all Da_2 of (64) that either

$$(2\beta_1+\nu\beta_2) \geqslant 0 \quad \text{.....} \quad (88a)$$

$$\mu\gamma_1\bar{\theta}\left[2(1+\beta_1)+\nu\beta_2\left(1+\frac{1}{4\mu}\right)\right]^2 < 4(\beta_2+\mu\gamma_1\bar{\theta}) * \\ * \left[1+(1+\beta_1)\left(2\beta_1+\nu\beta_2\left(1+\frac{1}{4\mu}\right)\right)+\beta_1(\beta_1+\nu\beta_2)\right] \tag{88b}$$

or

$$(2\beta_1+\nu\beta_2) < 0 \quad \text{.....} \quad (89a)$$

$$\mu\gamma_1\bar{\theta}\left(2+\frac{\nu\beta_2}{4\mu}\right)^2 < 4(\beta_2+\mu\gamma_1\bar{\theta})\left[1+(1+\beta_1)\left(\frac{\nu\beta_2}{4\mu}\right)-\beta_1^2\right] \tag{89b}$$

In (86a)-(89b), the following substitutions can be made:

$$\bar{\theta}=\begin{cases}\theta(y^{+}), & \beta_1>0,\ \beta_2<0 \qquad (90a)\\ \theta(y^{**}), & \beta_1<0,\ \beta_2>0 \qquad (90b)\end{cases}$$

$\bar{M}=M(y^{+})$ when $\beta_1>0,\ \beta_2<0$. (90c)

Since y^{+}, y^{**} must be determined numerically, it is clear that the uniqueness criteria (86a)-(89b) are impractical.

PROOF FOR

SUBPROBLEM II

WHEN $[1+(\gamma+\alpha)B]<0$ AND $B<0$

For subproblem II (γ =0), the following sufficient conditions for uniqueness for all values of Da_2 of (64) can be derived:

When $\beta_1>0$, $\beta_2<0$, require that

$$(\mu\gamma_1+\alpha\beta_2)<0 \quad \cdots\cdots\cdots\cdots \quad (91a)$$

$$\mu\gamma_1[2(1+\beta_1)+\alpha\beta_2]^2<4(\mu\gamma_1+\alpha\beta_2)*$$
$$*\left[1+\alpha\beta_2+2\beta_1(1+\beta_1)+\alpha\beta_1\bar{M}\right] \quad (91b)$$

where $\bar{M}$ is given by (79e).

When $\beta_1<0$, $\beta_2>0$, require that

$$\mu\gamma_1\left(\beta_2+\frac{2}{\alpha}\right)^2<4\left(\beta_2+\frac{\mu\gamma_1}{\alpha}\right)*$$
$$*\left[\frac{1}{\alpha}+\beta_2(1+\beta_1)-\frac{\beta_1(2\beta_1+\alpha\beta_2)-\beta_1\bar{M}^*}{\alpha}\right] \quad (92)$$

where $\bar{M}^*$ is given by (82c).

PROOF FOR

SUBPROBLEM I(i)

WHEN $[1+(\nu+\alpha)B]=0$ AND $B<0$

The steady state equation (64) becomes

$$\frac{1}{\mathcal{D}a_2}=\frac{X^{\mu}\left[(1+\alpha\beta_2-y)+\mathcal{D}a_1 X(1-y)\right]}{\left[(y-1)-\mathcal{D}a_1 X(1+\beta_1-y)\right]}\triangleq F(y) \tag{94}$$

Then, Lemma 3C1 can be applied and (68a)-(68b) yield

$$F'(y)=\begin{cases} <0,\ \beta_1<0,\beta_2>0,\ (1+\beta_1)<y^{**}<y<y_{\ell}<(1+\alpha\beta_2) & (95a)\\ >0,\ \beta_1>0,\beta_2<0,\ y^{+}<y<y^{**}<(1+\beta_1) & (95b)\end{cases}$$

Conditions (95a)-(95b) can be rewritten as

$$\beta_2 y^2+\mu\gamma_1(y-1)\Theta(y)\left\{y-1-\alpha\beta_2-\left[h_1(y)+h_2(y)\right]\right\}+$$

$$+\mu\gamma_1\beta_1 M(y)=\begin{cases} <0,\ \beta_1>0,\beta_2<0,\ y^{+}<y<y^{**} & (96a)\\ >0,\ \beta_1<0,\beta_2>0,\ y^{**}<y<y_{\ell} & (96b)\end{cases}$$

where

$$h_1(y) \triangleq \frac{-(\gamma+2\alpha)\beta_2}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)} = \begin{cases} >0\,, & \beta_1>0,\ \beta_2<0. \\ <0\,, & \beta_1<0,\ \beta_2>0. \end{cases} \tag{97a}$$

$$M(y) \triangleq \frac{(\mu-1)\alpha\beta_2\mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)\left[\alpha(1+\mathcal{D}a_1 X)+\gamma\mathcal{D}a_1 X\right]} \tag{97b}$$

$\Theta(y)$ and $h_2(y)$ are given by (70a), (70c) respectively.

When $\beta_1>0$, $\beta_2<0$, it suffices for uniqueness for all Da_2 of (94) that

$$(\mu\gamma_1+\alpha\beta_2)<0 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \tag{98a}$$

$$\mu\gamma_1\left[2-(\gamma+\alpha)\beta_2\right]^2<4(\mu\gamma_1+\alpha\beta_2)*$$
$$*\left[1+\alpha\beta_2-(\gamma+2\alpha)\beta_2(1+\beta_1)-\frac{\gamma\beta_1\beta_2}{4\mu}+\alpha\beta_1\bar{M}\right] \tag{98b}$$

where $\bar{M}$ is given by (79e). Observe that (98b) will never be satisfied.

When $\beta_1<0$, $\beta_2>0$, it suffices for uniqueness for all Da_2 of (94) that

$$\mu\gamma_1\left[2+\beta_2\left(\alpha+\frac{\nu}{4\mu}\right)\right]^2 < 4\left(\mu\gamma_1+\alpha\beta_2\right) * \\ * \left[1+\left(\alpha+\frac{\nu}{4\mu}\right)\beta_2(1+\beta_1)-\beta_1^2+\beta_1\overline{M^*}\right] \tag{99}$$

where $\bar{M}^*$ is given by (82c) with $\left[\beta_1+(\nu+\alpha)\beta_2\right]=0$.

PROOF FOR

SUBPROBLEM I(ii)

WHEN $\left[1+(\nu+\alpha)B\right]=0$ AND $B<0$

For subproblem I(ii) (α =0), we have that

$$\theta(y) \triangleq \frac{(1+\mathcal{D}a_1 X)}{\nu\mathcal{D}a_1 X} > 0 \quad \text{.....} \tag{100a}$$

$$h_1(y) \triangleq \frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)} = \begin{cases} >0\,, & \beta_1>0,\ \beta_2<0 \\ <0\,, & \beta_1<0,\ \beta_2>0 \end{cases} \tag{100b}$$

$$M(y) = 0 \quad \text{.....} \tag{100c}$$

$h_2(y)$ is given by (70c).

From (94) it follows that F(1)=0. (96a)-(96b) yield the following

$$\beta_2 y^2+\mu\gamma_1(y-1)\theta(y)\left\{y-1-\left[h_1(y)+h_2(y)\right]\right\}=$$

$$=\begin{cases}<0\ ,\ \beta_1>0,\ \beta_2<0\ ,\ 1<y<y^{**} & (101a)\\ >0\ ,\ \beta_1<0,\ \beta_2>0\ ,\ y^{**}<y<1 & (101b)\end{cases}$$

(101a)-(101b) can be rewritten as

$$\beta_2 y^2+\mu\gamma_1(y-1)^2\theta(y)-\mu\gamma_1(y-1)\theta(y)\left[h_1(y)+h_2(y)\right]=$$

$$=\begin{cases}<0\ ,\ \beta_1>0,\ \beta_2<0\ ,\ 1<y<y^{**} & (102a)\\ >0\ ,\ \beta_1<0,\ \beta_2>0,\ y^{**}<y<1 & (102b)\end{cases}$$

For (102a) to hold it suffices that

$$y^2\beta_2/\bar{\theta}+\mu\gamma_1(y-1)^2-\mu\gamma_1(y-1)(\underline{h_1}+\underline{h_2})<0 \qquad (103)$$
$$1<y<y^{**}$$

(103) can be rewritten as

$$y^2\left(\mu\gamma_1+\frac{\beta_2}{\bar{\theta}}\right)-y\mu\gamma_1(2+\underline{h_1}+\underline{h_2})+\mu\gamma_1(1+\underline{h_1}+\underline{h_2})<0 \qquad (104)$$
$$1<y<y^{**}$$

For (104) to hold it suffices that

$$(\mu\gamma_1 + \beta_2/\bar{\theta}) < 0 \quad \text{.....} \quad (105a)$$

$$\mu\gamma_1 (2 + \underline{h_1} + \underline{h_2})^2 < 4\left(\mu\gamma_1 + \frac{\beta_2}{\bar{\theta}}\right)(1 + \underline{h_1} + \underline{h_2}) \quad (105b)$$

The following substitutions can be made:

$$\underline{h_1} = h_1(1) = \beta_1 \Big/ \left(1 + \frac{1}{\mathcal{D}a_1}\right) \quad (106a)$$

$$\bar{\theta} = \theta(1) = (1 + \mathcal{D}a_1) / \nu \mathcal{D}a_1 \quad (106b)$$

$$\underline{h_2} = \nu\beta_2 / 4\mu \quad (106c)$$

Then (105a)-(105b) become

$$\left[\mu\gamma_1 + \frac{\nu\beta_2 \mathcal{D}a_1}{(1 + \mathcal{D}a_1)}\right] < 0 \quad (107a)$$

$$\mu\gamma_1\left[2+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}+\frac{\nu\beta_2}{4\mu}\right]^2<$$

$$<4\left[\mu\gamma_1+\frac{\nu\beta_2\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right]\left[1+\frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}+\frac{\nu\beta_2}{4\mu}\right] \tag{107b}$$

For (102b) to hold it suffices that

$$y^2\beta_2/\bar{\theta}+\mu\gamma_1(y-1)^2-\mu\gamma_1(y-1)(\underline{h_1}+\underline{h_2})>0 \tag{108}$$
$$y^{**}<y<1$$

(108) can be rewritten as

$$y^2\left(\mu\gamma_1+\frac{\beta_2}{\bar{\theta}}\right)-y\mu\gamma_1(2+\underline{h_1}+\underline{h_2})+\mu\gamma_1(1+\underline{h_1}+\underline{h_2})>0$$
$$y^{**}<y<1 \tag{109}$$

For (109) to hold it suffices that

$$\mu\gamma_1(2+\underline{h_1}+\underline{h_2})^2<4\left(\mu\gamma_1+\frac{\beta_2}{\bar{\theta}}\right)(1+\underline{h_1}+\underline{h_2}) \tag{110}$$

The following substitutions can be made:

$$\underline{h_1} = h_1(1) = \beta_1 \Big/ \left(1 + \frac{1}{\mathcal{D}a_1}\right) \tag{111a}$$

$$\underline{h_2} = 0 \tag{111b}$$

$$\overline{\theta} = \theta(1) = \frac{(1+\mathcal{D}a_1)}{\gamma\,\mathcal{D}a_1} \tag{111c}$$

Then, (110) becomes

$$\mu\gamma_1\left[2 + \frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}\right]^2 < 4\left[\mu\gamma_1 + \frac{\gamma\beta_2\mathcal{D}a_1}{(1+\mathcal{D}a_1)}\right] * \left[1 + \frac{\beta_1}{\left(1+\frac{1}{\mathcal{D}a_1}\right)}\right] \tag{112}$$

SUBCASE II: $[1+(\gamma+\alpha)B]>0$

Uniqueness and multiplicity criteria will be derived using the steady state equation (65) when $B \triangleq \beta_2/\beta_1 < 0$ for both subproblems I and II (see CHAPTER II). Figures will be presented first to acquire a feeling about the possible behavior of the system when $[1+(\gamma+\alpha)B]>0$.

The results of extensive numerical calculations are presented in figures 9 and 10, each of which describes six possible patterns of (65) when $B \triangleq \beta_2/\beta_1 < 0$ and $[1+(\gamma+\alpha)B]>0$. Figure 9 is for the case where $\alpha=0$.

Figures (9a)-(9b) and (10a)-(10b) describe the possible behavior of (65) when $\beta_1>0$, $\beta_2<0$, and $[1+(\gamma+\alpha)B]>0$. For cases (9a) and (10a) a unique steady state solution exists for all Da_1 of (65). For cases (9b) and (10b) a maximum of three solutions could occur for some range of Da_1. Since $\beta_2<0$, $\Phi(y)$ has one asymptote only.

Figures (9c)-(9f) and (10c)-(10f) describe the possible behavior of (65) when $\beta_1<0$, $\beta_2>0$ and $[1+(\gamma+\alpha)B]>0$. For cases (9c)-(9d) and (10c)-(10d) a unique steady state solution exists for all Da_1 of (65). For cases (9e)-(9f) and (10e) a maximum of three solutions could occur for some range of Da_1 values. For case (10f), $\Phi(y)$ has three asymptotes, multiplicity as a function

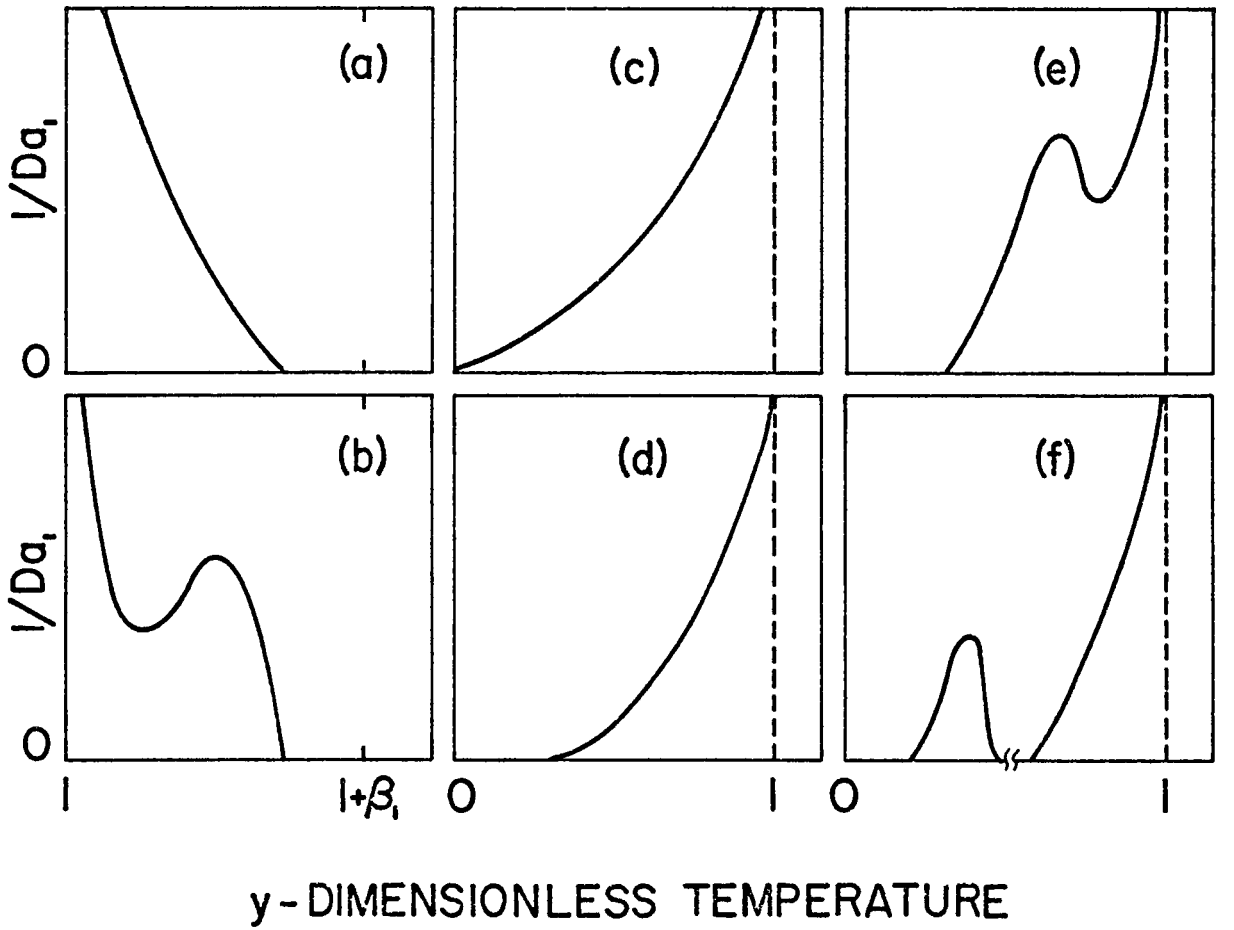


Figure 9: Various patterns of behavior when one reaction is endothermic and the other is exothermic in the case of subproblem I(ii).

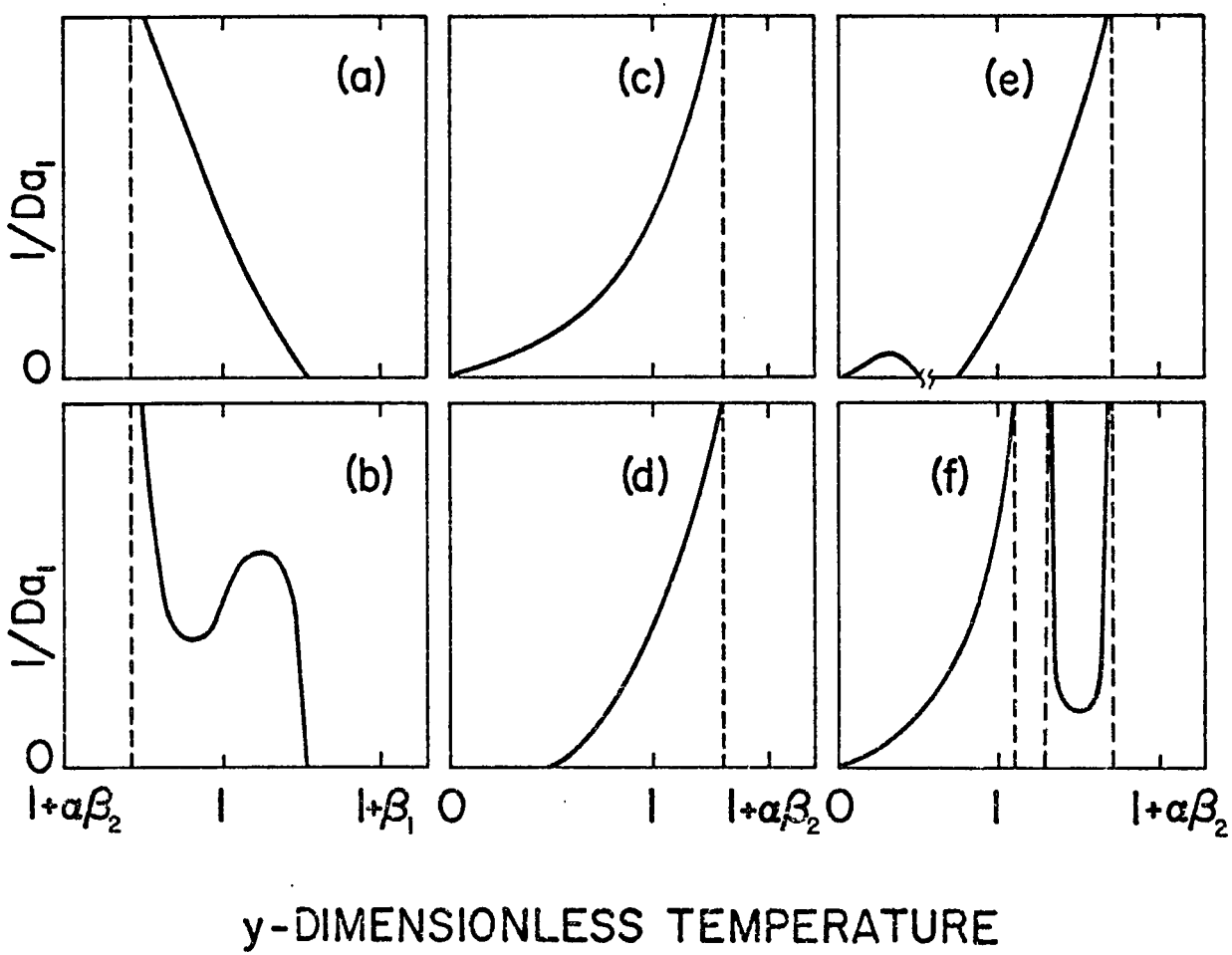


Figure 10: Various patterns of behavior when one reaction is endothermic and the other is exothermic in the case of subproblems I(i), II.

of Da_1 is of type 3-1, and there is an upper bound on $1/Da_1$ below which uniqueness is assured.

Our numerical calculations suggest that no more than three steady state solutions could occur when $B < 0$ and $[1+(\gamma+\alpha)B] > 0$, eventhough this result has not been proved analytically. Parametric values for figures 9 and 10 are presented in Appendix O.

1. Multiplicity criteria for subcase II

From figures 9 and 10, we are able to formulate the folllowing Lemmas concerning steady state multiplicity:

Lemma 3C5: Suppose that $\beta_1 > 0$, $\beta_2 < 0$. If equ. (114)

$$(1+\beta_1-y)+\mathcal{D}a_2 X^{\mu}[1+\beta_1+(\gamma+\alpha)\beta_2-y]=0 \qquad (114)$$

does not have multiple roots (see Appendix P), then it is possible to derive sufficient conditions for multiplicity for some Da_1 of (65), except that they are rather impractical, because they involve y_1 (the largest root of 114) which must be determined numerically (see figures (9b) and (10b)).

Lemma 3C6: Suppose that $\beta_1 < 0$, $\beta_2 > 0$. If the equation (115)

$$[(y-1)-\mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2-y)]=0 \qquad (115)$$

has only one root, then $\Phi(y)$ will have one asymptote, and a sufficient condition for multiplicity for some Da_1 of (65) is that (114) has multiple roots (as in figures (9f) and (10e)). If, however, (114) does not have multiple roots, then it is still possible to derive multiplicity criteria for some Da_1 of (65), except that they are rather impractical since they involve y* (the smallest root of (114)) which must be determined numerically (see figure (9e)). If (115) has multiple roots, then $\Phi(y)$ will have more than one asymptote and multiplicity will occur for some values of Da_1 (see figure (10f)). In this figure, the multiplicity as a function of Da_1 is of type 3-1, and there is an upper bound on $1/Da_1$ below which uniqueness is assured.

2. Uniqueness criteria for subcase II

From figures (9a),(10a), and (9c)-(9d), (10c)-(10d), we are able to formulate the following Lemma concerning uniqueness:

Lemma 3C7: Let Da_2 be such that the equation

$$\left[(y-1)-\mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2-y)\right]=0 \tag{117}$$

has one root only, y^{**}, and suppose that y_1 denotes the largest root of the equation

$$(1+\beta_1-y)+\mathcal{D}a_2 X^{\mu}[1+\beta_1+(\gamma+\alpha)\beta_2-y]=0 \tag{118}$$

Then, a necessary and sufficient condition for uniqueness for all Da_1 of (65) is

$$\Phi'(y)=\begin{cases} <0\ ,\ \beta_1>0\ ,\ \beta_2<0\ ,\ (1+\alpha\beta_2)<y^{**}<y<y_\ell<(1+\beta_1) & \text{(119a)} \\ >0\ ,\ \beta_1<0,\ \beta_2>0\ ,\ y^{+}<y<y^{**}<(1+\alpha\beta_2) & \text{(119b)} \end{cases}$$

where y^{+} is defined in Appendix Q.

Conditions (119a)-(119b) yield the following sufficient conditions for uniqueness for all Da_2 of (65):

(a) Subproblem I(i): ($\gamma \neq 0$, $\alpha \neq 0$)

When $\beta_1 > 0$, $\beta_2 < 0$, require that

$$\gamma_1 \bar{\theta}\left[2(1+\alpha\beta_2)+\beta_1+\frac{\gamma\beta_2(\mu+4)}{4}\right]^2 < 4(\beta_1+\gamma_1\bar{\theta}) * \\ * \left\{1+(1+\beta_1)\left[\beta_1+2\alpha\beta_2+\frac{\gamma\beta_2(\mu+4)}{4}\right]-\beta_1^2+\alpha\beta_2\bar{M}^*\right\} \quad (119c)$$

where $\bar{\theta}$ is given by (128a) and $\bar{M}^*$ by (128f).

When $\beta_1 < 0$, $\beta_2 > 0$, require that

$$(\beta_1+\gamma_1\bar{\theta}) < 0 \quad \cdots\cdots\cdots\cdots\cdots\cdots$$

$$\gamma_1\bar{\theta}(2+\beta_1)^2 < 4(\beta_1+\gamma_1\bar{\theta})\left\{1+\beta_1-\beta_1\left[2\alpha\beta_2+\frac{\gamma\beta_2(\mu+4)}{4}\right]+\alpha\beta_2\bar{M}^*\right\} \quad (119d)$$

The proofs for these uniqueness criteria are shown in the next section.

(b) Subproblem I(ii): ($\gamma \neq 0$, $\alpha = 0$)

When $\beta_1 > 0$, $\beta_2 < 0$, require that

$$\gamma_1\bar{\theta}(2+\beta_1)^2 < 4(\beta_1+\gamma_1\bar{\theta})(1+\beta_1) \quad (119e)$$

where $\bar{\theta}$ is given by (139).

When $\beta_1 < 0$, $\beta_2 > 0$, require that

$$(\beta_1+\gamma_1\bar{\theta}) < 0 \quad (119f)$$

$$\gamma_1\bar{\theta}\left[2+\beta_1+\frac{\gamma\beta_2(\mu+4)}{4}\right]^2 < 4(\beta_1+\gamma_1\bar{\theta})\left[1+\beta_1+\frac{\gamma\beta_2(\mu+4)}{4}\right] \quad (119g)$$

where $\overline{\theta}$ is given by (141).

The proofs for (138), (140a)-(140b) are shown in the next section.

(c) Subproblem II: ($\gamma \equiv 0$, $\alpha \neq 0$)

See page 96.

This concludes Lemma 3C7 on uniqueness.

The next section contains proofs for all the uniqueness conditions shown above which follow from Lemma 3C7.

PROOFS OF THE UNIQUENESS CRITERIA FOR SUBCASE II: $[1+(\gamma+\alpha)B]>0$

PROOF

FOR SUBPROBLEM I(i)

WHEN $[1+(\nu+\alpha)B]>0$ AND $B<0$

(119a)-(119b) can be rewritten as

$$\beta_1 y^2+\gamma_1(y-1)\Theta(y)\left\{(y-1-\beta_1)-[h_1(y)+h_2(y)]\right\}+$$

$$+\gamma_1\alpha\beta_2[M_1(y)+M_2(y)]=\begin{cases}>0\,,\ \beta_1>0,\beta_2<0,\ y^{**}<y<y_\ell & \text{(120a)}\\ <0\,,\ \beta_1<0,\beta_2>0,\ y^{+}<y<y^{**} & \text{(120b)}\end{cases}$$

where

$$\Theta(y)\triangleq\frac{(1+\mathcal{D}a_2X^\mu)}{[1+(1+\nu B)\mathcal{D}a_2X^\mu]}>0 \qquad \text{(121a)}$$

$$h_1(y)\triangleq\frac{2\alpha\beta_2\,\mathcal{D}a_2X^\mu}{(1+\mathcal{D}a_2X^\mu)}=\begin{Bmatrix}<0,\ \beta_1>0,\ \beta_2<0\\ >0,\ \beta_1<0,\ \beta_2>0\end{Bmatrix} \qquad \text{(121b)}$$

$$h_2(y)\triangleq\frac{\nu\beta_2[\mu+(1+\mathcal{D}a_2X^\mu)]\,\mathcal{D}a_2X^\mu}{(1+\mathcal{D}a_2X^\mu)^2}=\begin{Bmatrix}<0,\ \beta_1>0,\beta_2<0\\ >0,\ \beta_1<0,\beta_2>0\end{Bmatrix} \qquad \text{(121c)}$$

$$M_1(y) \triangleq \frac{-(\mu-1)\,\beta_1\,\mathcal{D}a_2\,X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})\left[1+(1+\nu B)\mathcal{D}a_2 X^{\mu}\right]} \tag{121d}$$

$$M_2(y) \triangleq \frac{\left[\beta_1+(\nu+\alpha)\beta_2\right]\left(\mathcal{D}a_2 X^{\mu}\right)^2}{(1+\mathcal{D}a_2 X^{\mu})\left[1+(1+\nu B)\mathcal{D}a_2 X^{\mu}\right]} =$$

$$= \begin{cases} >0\ , & \beta_1>0,\ \beta_2<0 \\ <0\ , & \beta_1<0,\ \beta_2>0 \end{cases} \tag{121e}$$

Since the sign of (y-1) is not known, we prefer to rewrite (120a)-(120b) as

$$\beta_1 y^2+\gamma_1(y-1)^2\theta(y)-\gamma_1\theta(y)(y-1-\beta_1+\beta_1)\left[\beta_1+h_1(y)+h_2(y)\right]+$$

$$+\gamma_1\alpha\beta_2\left[M_1(y)+M_2(y)\right]=$$

$$= \begin{cases} >0\ , & \beta_1>0,\ \beta_2<0,\ y^{**}<y<y_{\ell} \qquad (122a) \\ <0\ , & \beta_1<0,\ \beta_2>0,\ y^{+}<y<y^{**} \qquad (122b) \end{cases}$$

For (122a) to hold it suffices that

$$y^2(\beta_1+\gamma_1\bar{\theta})-y\gamma_1\bar{\theta}(2+\beta_1+\underline{h}_1+\underline{h}_2)+$$
$$+\gamma_1\bar{\theta}\left[1+(1+\beta_1)(\beta_1+\underline{h}_1+\underline{h}_2)-\beta_1(\beta_1+\bar{h}_1+\bar{h}_2)+\alpha\beta_2\bar{M}^*\right]>0$$
$$y^{**}<y<y_\ell \tag{123}$$

For (122b) to hold it suffices that

$$y^2(\beta_1+\gamma_1\bar{\theta})-y\gamma_1\bar{\theta}(2+\beta_1+\underline{h}_1+\underline{h}_2)+$$
$$+\gamma_1\bar{\theta}\left[1+(1+\beta_1)(\beta_1+\underline{h}_1+\underline{h}_2)-\beta_1(\beta_1+\bar{h}_1+\bar{h}_2)+\alpha\beta_2\bar{M}^*\right]<0 \tag{124}$$
$$y^{+}<y<y^{**}$$

In (123)-(124) we denote

$$M^*(y)\triangleq\frac{M_1(y)+M_2(y)}{\theta(y)} \tag{125}$$

For (123) to hold it suffices that

$$\gamma_1\bar{\theta}(2+\beta_1+\underline{h_1}+\underline{h_2})^2<4(\beta_1+\gamma_1\bar{\theta})*$$

$$*\left[1+(1+\beta_1)(\beta_1+\underline{h_1}+\underline{h_2})-\beta_1(\beta_1+\bar{h}_1+\bar{h}_2)+\alpha\beta_2\overline{M}^*\right] \quad (126)$$

For (124) to hold it suffices that

$$(\beta_1+\gamma_1\bar{\theta})<0 \quad (127a)$$

$$\gamma_1\bar{\theta}(2+\beta_1+\underline{h_1}+\underline{h_2})^2<4(\beta_1+\gamma_1\bar{\theta})*$$

$$*\left[1+(1+\beta_1)(\beta_1+\underline{h_1}+\underline{h_2})-\beta_1(\beta_1+\bar{h}_1+\bar{h}_2)+\alpha\beta_2\overline{M}^*\right] \quad (127b)$$

The following substitutions can be made:

$$\bar{\theta}=\begin{cases}\theta(1+\beta_1), & \beta_1>0,\ \beta_2<0\\ \theta(1+\alpha\beta_2), & \beta_1<0,\ \beta_2>0\end{cases} \quad (128a)$$

$$\underline{h_1}=\begin{cases}2\alpha\beta_2, & \beta_1>0,\ \beta_2<0\\ 0, & \beta_1<0,\ \beta_2>0\end{cases} \quad (128b)$$

$$\bar{h}_1 = \begin{cases} 0 \ , & \beta_1 > 0 \ , \ \beta_2 < 0 \\ 2\alpha\beta_2 \ , & \beta_1 < 0 \ , \ \beta_2 > 0 \end{cases} \tag{128c}$$

$$\underline{h_2} = \begin{cases} \nu\beta_2(\mu+4)/4 \ , & \beta_1 > 0, \beta_2 < 0 \\ 0 \ , & \beta_1 < 0, \beta_2 > 0 \end{cases} \tag{128d}$$

$$\bar{h}_2 = \begin{cases} 0 \ , & \beta_1 > 0 \ , \ \beta_2 < 0 \\ \nu\beta_2(\mu+4)/4 \ , & \beta_1 < 0 \ , \ \beta_2 > 0 \end{cases} \tag{128e}$$

$$\overline{M^*} = \begin{cases} [\beta_1 + (\nu+\alpha)\beta_2] \ , & \beta_1 > 0, \beta_2 < 0 \ , \ \mu \geqslant 1 \\ [\beta_1 + (\nu+\alpha)\beta_2] + \dfrac{(1-\mu)\beta_1}{2} \ , & \beta_1 > 0, \beta_2 < 0, \mu < 1 \\ \dfrac{(1-\mu)\beta_1}{2} \ , & \beta_1 < 0, \beta_2 > 0 \ , \ \mu \geqslant 1 \\ 0 \ , & \beta_1 < 0, \beta_2 > 0 \ , \ \mu < 1 \end{cases} \tag{128f}$$

Using (128a)-(128f), condition (126) becomes

$$\gamma_1\bar{\theta}\left[2(1+\alpha\beta_2)+\beta_1+\frac{\nu\beta_2(\mu+4)}{4}\right]^2<4(\beta_1+\gamma_1\bar{\theta})*$$

$$*\left\{1+(1+\beta_1)\left[\beta_1+2\alpha\beta_2+\frac{\nu\beta_2(\mu+4)}{4}\right]-\beta_1^2+\alpha\beta_2\bar{M}^*\right\} \quad (129)$$

and conditions (127a)-(127b) become

$$(\beta_1+\gamma_1\bar{\theta})<0 \quad (130a)$$

$$\gamma_1\bar{\theta}(2+\beta_1)^2<4(\beta_1+\gamma_1\bar{\theta})\left\{1+\beta_1-\beta_1\left[2\alpha\beta_2+\frac{\nu\beta_2(\mu+4)}{4}\right]+\alpha\beta_2\bar{M}^*\right\} \quad (130b)$$

PROOF

FOR SUBPROBLEM I(ii)

WHEN $[1+(\nu+\alpha)B]>0$ AND $B<0$

Consider subproblem I(ii) (α =0). Then, the steady state equation (65) becomes

$$\frac{1}{\mathcal{D}a_1}=\frac{X\left\{(1+\beta_1-y)+\mathcal{D}a_2X^{\mu}(1+\beta_1+\nu\beta_2-y)\right\}}{(y-1)\left(1+\mathcal{D}a_2X^{\mu}\right)}\triangleq\Phi(y) \tag{131}$$

and (119a)-(119b) yield

$$\Phi'(y)=\begin{cases}<0\ , & \beta_1>0\ ,\ \beta_2<0\ ,\ 1<y<y_{\ell}<(1+\beta_1) \quad (132a)\\ >0\ , & \beta_1<0\ ,\ \beta_2>0\ ,\ y^{+}<y<1 \quad (132b)\end{cases}$$

Conditions (120a)-(120b) become

$$\beta_1y^2+\gamma_1(y-1)\,\Theta(y)\left[(y-1-\beta_1)-h_2(y)\right]=$$

$$=\begin{cases}>0\ , & \beta_1>0\ ,\ \beta_2<0\ ,\ 1<y<y_{\ell} \quad (133a)\\ <0\ , & \beta_1<0\ ,\ \beta_2>0\ ,\ y^{+}<y<1 \quad (133b)\end{cases}$$

where $\theta(y)$ and $h_2(y)$ are given by (121a), (121c) respectively.

For (133a) to hold it suffices that

$$\beta_1 y^2 + \gamma_1 \bar{\theta}(y-1)^2 - \gamma_1 \bar{\theta}(y-1)(\beta_1 + \bar{h}_2) > 0 \qquad (134)$$

$$1 < y < y_\ell$$

(134) can be rewritten as

$$y^2(\beta_1 + \gamma_1 \bar{\theta}) - y\gamma_1 \bar{\theta}(2 + \beta_1 + \bar{h}_2) + \gamma_1 \bar{\theta}(1 + \beta_1 + \bar{h}_2) > 0 \qquad (135)$$

$$1 < y < y_\ell$$

For (135) to hold it suffices that

$$\gamma_1 \bar{\theta}(2 + \beta_1 + \bar{h}_2)^2 < 4(\beta_1 + \gamma_1 \bar{\theta})(1 + \beta_1 + \bar{h}_2) \qquad (136)$$

Similarly, we find that for (133b) to hold it suffices that

$$(\beta_1+\gamma_1\bar{\theta})<0 \tag{137a}$$

$$\gamma_1\bar{\theta}(2+\beta_1+\bar{h}_2)^2<4(\beta_1+\gamma_1\bar{\theta})(1+\beta_1+\bar{h}_2) \tag{137b}$$

Using (128e), condition (136) becomes

$$\gamma_1\bar{\theta}(2+\beta_1)^2<4(\beta_1+\gamma_1\bar{\theta})(1+\beta_1) \tag{138}$$

where

$$\bar{\theta}=\theta(1+\beta_1) \tag{139}$$

Using (128e), conditions (137a)-(137b) become

$$(\beta_1+\gamma_1\bar{\theta})<0 \tag{140a}$$

$$\gamma_1\bar{\theta}\left[2+\beta_1+\frac{\nu\beta_2(\mu+4)}{4}\right]^2<4(\beta_1+\gamma_1\bar{\theta})\left[1+\beta_1+\frac{\nu\beta_2(\mu+4)}{4}\right] \tag{140b}$$

where

$$\bar{\theta}=\theta(1)=\frac{(1+\mathcal{D}a_2)}{\left[1+(1+\nu B)\mathcal{D}a_2\right]} \tag{141}$$

PROOF

FOR SUBPROBLEM II

WHEN $[1+(\nu+\alpha)B]>0$ AND $B<0$

For subproblem II ($\nu \equiv 0$), condition (129) becomes

$$\gamma_1[2(1+\alpha\beta_2)+\beta_1]^2 < 4(\beta_1+\gamma_1) * \\ * [1+(1+\beta_1)(\beta_1+2\alpha\beta_2)-\beta_1^2+\alpha\beta_2\overline{M}^*] \tag{142}$$

while conditions (130a)-(130b) become

$$(\beta_1+\gamma_1) < 0 \tag{143a}$$

$$\gamma_1(2+\beta_1)^2 < 4(\beta_1+\gamma_1)[1+\beta_1-2\alpha\beta_2\beta_1+\alpha\beta_2\overline{M}^*] \tag{143b}$$

where $\bar{M}^*$ is given by (128f).

CHAPTER IV

CONCLUSIONS

The purpose of this work was to examine the possible behavior of lumped parameter systems in which either two consecutive first order chemical reactions $A \longrightarrow B \longrightarrow C$ or two independent first order chemical reactions $A \longrightarrow P_1$, $B \longrightarrow P_2$ occur.

We found that there is a great similarity in the way the system behaves for these two chemical reaction schemes. From the mathematical point of view, $A \longrightarrow P_1$, $B \longrightarrow P_2$ can be represented as a special case of $A \longrightarrow B \longrightarrow C$.

We proved that when both reactions are endothermic, a unique steady state solution exists for either of the two reaction schemes. Uniqueness is also assured when one reaction is endothermic and the other is isothermal. When both reactions are isothermal, then y=1 is the only solution of the steady state equation.

When the first reaction is exothermic and the second is isothermal, the system degenerates to the case of a single chemical reaction. Uniqueness and multiplicity criteria have already been derived for the case of a single chemical reaction [3-5], and we know that a maximum of three steady state solutions may occur for a bounded range of the Damkohler number.

When both reactions are exothermic, a maximum of FIVE steady

state solutions may occur, and we derived sufficient conditions for the existence of these five solutions. Multiplicity may exist over an unbounded range of Damkohler numbers. Very simple, sufficient conditions for multiplicity have been derived. Sufficient conditions for uniqueness were developed using various forms of the steady state equation. We found the surprising result that five steady state solutions may exist when the first reaction is isothermal and the second is exothermic.

When one reaction is exothermic and the other is endothermic, a maximum of three steady state solutions may occur, and the existence of steady state multiplicity over an unbounded range of Damkohler numbers has been demonstrated numerically. Conservative, sufficient conditions for uniqueness have been derived using two different forms of the steady state equation interchangeably. Very simple, sufficient conditions for multiplicity have been derived.

Extensive numerical calculations were carried-out for different sets of parametric values in order to examine the possible behavior of the system for the two reaction schemes. These calculations were performed using various forms of the steady state equation, and the results have been presented in the figures.

As in the work of Chen and Luss [12], we also conclude that it is very dangerous to predict the qualitative behavior of a system in which a complex reaction network occurs from an

analysis of a simpler reaction scheme. In our problem, however, when both reactions are endothermic, a unique steady state solution exists and this is in agreement with the case of a single chemical reaction occuring in a lumped parameter system. Another result of our work is the derivation of sufficient conditions for the existence of steady state multiplicity for ALL values of Da_2 when both reactions are exothermic. This is a powerful result which has not been previously reported.

When these reactions occur inside a porous catalytic pellet, a distributed parameter model which accounts for intra-particle gradients must be used. Based on information for the case of a single, exothermic chemical reaction, it should be mentioned that the structure of the solutions for distributed parameter systems may be more intricate. It is expected, however, that certain similarities will exist for both the lumped and the distributed parameter model in which the same chemical reactions occur.

Experiments should be performed for both reaction schemes, in order to verify our theoretical results. Especially since there are very few studies reported on the two independent first order chemical reactions $A \longrightarrow P_1$, $B \longrightarrow P_2$. A logical extension of our work would be to examine the behavior of more complicated reaction schemes such as the one by McGreavy and Thornton [23-24].

NOMENCLATURE

English Characters

A: Species A, or concentration of species A.

B: Species B, or concentration of species B.

C: Species C...../ C_p: Heat capacity.

D: Species D...../ Da_i: Damkohler number.

E_i: Activation energy.

F(y): Defined by (21).

g(y): Defined by (42a).

h: Heat transfer coefficient.

k_{ca}, k_{cB}: Mass transfer coefficients for species A,B.

k_i: Reaction rate.

P_1, P_2: Species P_1, P_2.

q: Volumetric flow rate of feed.

R: Universal gas constant.

S_x: External surface area of catalytic pellet.

T: Temperature.

V: Volume of the reactor

V_p: Volume of catalytic pellet.

X: Defined by (5d).

y: Dimensionless temperature.

y** : Values of y at which the steady state equation has an asymptote.

Greek Characters

α : Defined by (8).

β_i : Dimensionless heat of reaction defined by (5g).

γ_i : Dimensionless activation energy defined by (5a).

δ : Quantity defined on page 38.

(ΔH_i) : Heat of reaction.

ε_p : Porosity of catalytic pellet.

$Z(y)$: Function defined by (42).

λ : Defined by (34b).

μ : Ratio of activation energies, defined by (5b).

ν : Ratio of mass transfer coefficients, defined by (5e).

σ : Ratio of Damkohler numbers, defined by (41a).

υ : Defined by (14).

$\Phi(y)$: Function defined by (33).

Symbols in Script

$\mathcal{H}(y)$: Defined by (45a).

Subscripts

0: Conditions in the bulk, or inlet conditions.

s: Conditions at steady state.

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APPENDICES

APPENDIX A

Consider two consecutive first order reactions $A \longrightarrow B \longrightarrow C$ occuring in a homogeneous ideal CSTR. Then, the following steady state species and energy conservation equations apply:

$$q(A_o - A_s) = V K_1 A_s \tag{A1}$$

$$q(B_s - B_o) = V(K_1 A_s - K_2 B_s) \tag{A2}$$

$$q \rho C_p (T - T_o) = (-\Delta H_1) V K_1 A_s + (-\Delta H_2) V K_2 B_s \tag{A3}$$

Using equs. (4)-(5d) and letting

$$\mathcal{D}a_1 = \frac{V K_1(T_o)}{q}, \quad \mathcal{D}a_2 = \frac{V K_2(T_o)}{q} \tag{A4}$$

$$\beta_1 = \frac{(-\Delta H_1) A_o}{\rho C_p T_o}, \quad \beta_2 = \frac{(-\Delta H_2) A_o}{\rho C_p T_o}, \quad \alpha = (B_o / A_o) \tag{A5}$$

allows us to rewrite (A1)-(A2) as

$$\left(\frac{A_s}{A_o}\right) = \frac{1}{(1 + \mathcal{D}a_1 X)} \tag{A6}$$

$$\left(\frac{B_s}{A_o}\right) = \frac{1}{(1 + \mathcal{D}a_2 X^{\mu})} \left[\alpha + \frac{\mathcal{D}a_1 X}{(1 + \mathcal{D}a_1 X)}\right] \tag{A7}$$

Using (4)-(5d), (A4)-(A5), and substituting (A6)-(A7) into equ. (A3) finally yields

$$(y-1)=\beta_1\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}+\beta_2\frac{\mathcal{D}a_2 X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})}\left[\alpha+\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}\right] \quad \text{(A8)}$$

Equ. (A8) results from (9) by letting $\gamma=1$.

Consider two consecutive first order reactions $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ occuring on a catalytic wire. Then, the following steady state species and energy conservation equations apply:

$$K_{ca}(A_o-A_s)=K_1 A_s \quad \text{(A9)}$$

$$K_{cB}(B_s-B_o)=(K_1 A_s-K_2 B_s) \quad \text{(A10)}$$

$$h(T-T_o)=(-\Delta H_1)K_1 A_s+(-\Delta H_2)K_2 B_s \quad \text{(A11)}$$

Using equs. (4)-(5e) and letting

$$\mathcal{D}a_1 = \frac{K_1(T_0)}{K_{ca}} \quad , \quad \mathcal{D}a_2 = \frac{K_2(T_0)}{K_{cB}} \tag{A12}$$

$$\beta_1 = \frac{(-\Delta H_1) K_{ca} A_0}{h T_0} \, , \beta_2 = \frac{(-\Delta H_2) K_{cB} A_0}{h T_0} \, , \quad \alpha = (B_0 / A_0) \tag{A13}$$

allows us to rewrite (A9)-(A10) as

$$\left(\frac{A_s}{A_0}\right) = \frac{1}{(1 + \mathcal{D}a_1 X)} \tag{A14}$$

$$\left(\frac{B_s}{A_0}\right) = \frac{1}{(1 + \mathcal{D}a_2 X^{\mu})} \left[\alpha + \frac{\gamma \mathcal{D}a_1 X}{(1 + \mathcal{D}a_1 X)}\right] \tag{A15}$$

Using equs. (4)-(5e) and substituting (A14)-(A15) into (A11) yields equ. (9).

APPENDIX B

Suppose that two independent first order chemical reactions $A \xrightarrow{K_1} P_1$, $B \xrightarrow{K_2} P_2$, occur in a porous catalytic pellet. Assuming that intra-particle temperature and concentration gradients are negligible, allows us to write the following species and energy conservation equations:

$$\varepsilon_p K_{ca} S_x (A_o - A_s) = V_p K_1 A_s \tag{B1}$$

$$\varepsilon_p K_{cB} S_x (B_o - B_s) = V_p K_2 B_s \tag{B2}$$

$$h S_x (T - T_o) = (-\Delta H_1) V_p K_1 A_s + (-\Delta H_2) V_p K_2 B_s \tag{B3}$$

Using equs. (4)-(5g), we can rewrite (B1)-(B2) as

$$\left(\frac{A_s}{A_o}\right) = \frac{1}{(1 + \mathcal{D}a_1 X)} \tag{B4}$$

$$\left(\frac{B_s}{A_o}\right) = \frac{\alpha}{(1 + \mathcal{D}a_2 X^{\mu})} \tag{B5}$$

Substituting (B4)-(B5) and using equs. (4)-(5g) into (B3) yields

$$(y-1)=\beta_1\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}+\alpha\beta_2\frac{\mathcal{D}a_2 X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})} \qquad \text{(B6)}$$

Observe that (B6) results from equ. (9) if we set $\gamma \equiv 0$. This is also true for other lumped parameter systems, such as catalytic wires and homogeneous ideal CSTR's.

APPENDIX C

From (24d) we find that

$$\frac{dM(y)}{dy}=\frac{[\mu(\beta_1+\nu\beta_2)+\alpha\beta_2]\nu(\mathcal{D}a_1\mathbb{X})^2+[\mu(\beta_1+\nu\beta_2)+\alpha\beta_2]\alpha\mathcal{D}a_1\mathbb{X}(1+\mathcal{D}a_1\mathbb{X})}{\mu^2(1+\mathcal{D}a_1\mathbb{X})^2[\alpha+(\nu+\alpha)\mathcal{D}a_1\mathbb{X}]^2(y^2/\mu\gamma_1\mathcal{D}a_1\mathbb{X})}$$

$$+\frac{\{\mu\mathcal{D}a_1\mathbb{X}[\beta_1+(\nu+\alpha)\beta_2]+(\mu-1)\alpha\beta_2\}\alpha(1+\mathcal{D}a_1\mathbb{X})}{\mu^2(1+\mathcal{D}a_1\mathbb{X})^2[\alpha+(\nu+\alpha)\mathcal{D}a_1\mathbb{X}]^2(y^2/\mu\gamma_1\mathcal{D}a_1\mathbb{X})}$$

If

$$\mu\mathcal{D}a_1[\beta_1+(\nu+\alpha)\beta_2]+(\mu-1)\alpha\beta_2\geqslant 0$$

then

$$dM(y)/dy>0\Rightarrow \underline{M}=M(y^{**})\geqslant M(1)$$

If

$$\mu\mathcal{D}a_1[\beta_1+(\nu+\alpha)\beta_2]+(\mu-1)\alpha\beta_2<0$$

then from (24d) it follows that

$$\mu\mathcal{D}a_1\mathbb{X}(y)[\beta_1+(\nu+\alpha)\beta_2]+(\mu-1)\alpha\beta_2>$$

$$>\mu\mathcal{D}a_1[\beta_1+(\nu+\alpha)\beta_2]+(\mu-1)\alpha\beta_2\,,\ 1\leq y^{**}<y<y^{*}$$

Consequently, for both cases we find that

$$M(y)>M(1)\ .$$

From (24c) we find that

$$\frac{d}{dy}\left[\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)^2}\right] = 0$$

when

$$(\mathcal{D}a_1 X) = 1$$

Therefore $h_2(y)$ has its maximum

$$\max_{0<y} h_2(y) = \left(\frac{\gamma\beta_2}{4\mu}\right)$$

at points satisfying the equation

$$e^{\gamma_1\left(1-\frac{1}{y}\right)} = 1/\mathcal{D}a_1 \quad .$$

APPENDIX D

Consider subproblem I(ii). For this subproblem, equ. (33) takes the form

$$\frac{1}{Da_1} = \frac{X\left\{(1+\beta_1-y) + Da_2 X^{\mu}(1+\beta_1+\gamma\beta_2-y)\right\}}{(y-1)(1+Da_2 X^{\mu})} \triangleq \Phi(y) \qquad \text{(D1)}$$

Lemma D1: A necessary and sufficient condition for uniqueness for all Da_1 of equ. (D1) is

$$d\Phi(y)/dy < 0 \qquad \text{(D2)}$$

where $1 < y < y_m < (1+\beta_1+\gamma\beta_2)$ and y_m is the largest root of the equation

$$(1+\beta_1-y) + Da_2 X^{\mu}(1+\beta_1+\gamma\beta_2-y) = 0 \qquad \text{(D3)}$$

Using the steady state equation (D1) , condition (D2) yields

$$\gamma_1(y-1)\frac{(1+Da_2 X^{\mu})}{[1+(1+\gamma B)Da_2 X^{\mu}]}\left\{\beta_1 + \frac{\gamma\beta_2 Da_2 X^{\mu}}{(1+Da_2 X^{\mu})} + \right.$$

$$\left. + \frac{\mu\gamma\beta_2 Da_2 X^{\mu}}{(1+Da_2 X^{\mu})^2} - (y-1)\right\} - \beta_1 y^2 < 0 \qquad \text{(D4)}$$

where $1 < y < y_m$.

Or

$$\beta_1 y^2 + \gamma_1 (y-1) \frac{(1+\mathcal{D}a_2 X^\mu)}{[1+(1+\nu B)\mathcal{D}a_2 X^\mu]} \left\{ (y-1) - \beta_1 - \frac{\nu \beta_2 \mathcal{D}a_2 X^\mu}{(1+\mathcal{D}a_2 X^\mu)} - \right.$$

$$\left. - \frac{\mu \nu \beta_2 \mathcal{D}a_2 X^\mu}{(1+\mathcal{D}a_2 X^\mu)^2} \right\} > 0 \qquad \text{(D5)}$$

where $1 < y < y_m$.

Or

$$\beta_1 y^2 + \gamma_1 (y-1) \Theta(y) \left\{ (y-1) - \left(\beta_1 + h_1(y) + h_2(y) \right) \right\} > 0 \qquad \text{(D6)}$$

where $1 < y < y_m$ and

$$\Theta(y) \triangleq \frac{(1+\mathcal{D}a_2 X^\mu)}{[1+(1+\nu B)\mathcal{D}a_2 X^\mu]} > 0 \qquad \text{(D7a)}$$

$$h_1(y) \triangleq \frac{\gamma \beta_2 \mathcal{D}a_2 X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})} > 0 \qquad \text{(D7b)}$$

$$h_2(y) \triangleq \frac{\mu \gamma \beta_2 \mathcal{D}a_2 X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})^2} > 0 \qquad \text{(D7c)}$$

For (D6) to hold, it suffices that

$$\beta_1 y^2 + \gamma_1 (y-1)\bar{\theta}\left[(y-1) - (\beta_1 + \bar{h}_1 + \bar{h}_2)\right] > 0 \qquad \text{(D8)}$$

where $1 < y < y_m$.

Condition (D8) can be rewritten as

$$y^2(\beta_1 + \gamma_1\bar{\theta}) - y\gamma_1\bar{\theta}\left[2 + \beta_1 + \bar{h}_1 + \bar{h}_2\right] + \gamma_1\bar{\theta}(1 + \beta_1 + \bar{h}_1 + \bar{h}_2) > 0 \qquad \text{(D9)}$$

where $1 < y < y_m < (1 + \beta_1 + \gamma\beta_2)$.

For (D9) to hold, it suffices that

$$\gamma_1 \bar{\theta}\left(2+\beta_1+\bar{h}_1+\bar{h}_2\right)^2 < 4\left(\beta_1+\gamma_1\bar{\theta}\right)\left(1+\beta_1+\bar{h}_1+\bar{h}_2\right) \tag{D10}$$

Condition (D10) is sufficient for uniqueness for all Da_1 values of equ. (D1). Observe that when $Da_2=0$, then (D10) degenerates to $\beta_1\gamma_1 < 4(1+\beta_1)$.

From (D7b) we have that

$$\frac{dh_1(y)}{dy} = \frac{\nu\beta_2\left(\frac{X^{-\mu}}{\mathcal{D}a_2}\right)\left(\frac{\mu\gamma_1}{y^2}\right)}{\left(1+\frac{1}{\mathcal{D}a_2 X^{\mu}}\right)^2} > 0 \tag{D11}$$

Consequently,

$$\bar{h}_1 = h_1(y_m) \tag{D12}$$

From (D7c) we find that

$$h_2(y) = \frac{\mu\nu\beta_2}{\left(2+\mathcal{D}a_2 X^{\mu}+\frac{1}{\mathcal{D}a_2 X^{\mu}}\right)} \tag{D13}$$

Thus, we can use

$$\bar{h}_2 = (\mu \nu \beta_2 / 4) \tag{D14}$$

From (D7a) we have that

$$\theta(y) = \frac{1}{\left[1 + \dfrac{\nu B}{\left(1 + \dfrac{1}{\mathcal{D}a_2 X^{\mu}}\right)}\right]} \tag{D15}$$

Therefore,

$$\frac{d\theta(y)}{dy} = -\frac{\nu B \left(\dfrac{X^{-\mu}}{\mathcal{D}a_2}\right)\left(\dfrac{\mu \gamma_1}{y^2}\right)}{\left[1 + \dfrac{\nu B}{\left(1 + \dfrac{1}{\mathcal{D}a_2 X^{\mu}}\right)}\right]^2 \left(1 + \dfrac{1}{\mathcal{D}a_2 X^{\mu}}\right)^2} < 0 \tag{D16}$$

from which it follows that

$$\bar{\theta} = \theta(1) = \frac{(1 + \mathcal{D}a_2)}{\left[1 + (1 + \nu B)\mathcal{D}a_2\right]} \tag{D17}$$

A simpler uniqueness condition can be obtained if instead of (D12) we use

$$\bar{h}_1 = \nu\beta_2 \tag{D18}$$

Substituting (D14), (D17) and (D18) into (D10) yields

$$\frac{\gamma_1(1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]}\left(2+\beta_1+\nu\beta_2+\frac{\mu\nu\beta_2}{4}\right)^2 <$$

$$< 4\left[\beta_1+\frac{\gamma_1(1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]}\right]\left(1+\beta_1+\nu\beta_2+\frac{\mu\nu\beta_2}{4}\right) \tag{D19}$$

(D19) can be rewritten as

$$\frac{\gamma_1(1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]}\left[\beta_1+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right]^2 <$$

$$< 4\beta_1\left[1+\beta_1+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right] \tag{D20}$$

A uniqueness condition which is simpler than (D20) can be obtained if instead of (D17) we use

$$\bar{\Theta} = 1 \tag{D21}$$

Then, (34) follows directly from (D20).

APPENDIX E

Equ. (36), which follows directly from the steady state equ. (9), can be rewritten as

$$1 = F_1(y) + F_2(y) + F_3(y) \tag{E1}$$

where

$$F_1(y) \triangleq \frac{\mathcal{D}a_1 X (1+\beta_1-y)}{(y-1)} \tag{E2a}$$

$$F_2(y) \triangleq \frac{\mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2-y)}{(y-1)} \tag{E2b}$$

$$F_3(y) \triangleq \frac{\mathcal{D}a_1 \mathcal{D}a_2 X^{\mu+1}[1+\beta_1+(\gamma+\alpha)\beta_2-y]}{(y-1)} \tag{E2c}$$

Lemma E1: A necessary and sufficient condition for the monotonicity of $F_3(y)$ for all values of $(Da_1 * Da_2)$ in the interval $(1,\ 1+\beta_1+(\gamma+\alpha)\beta_2)$ is

$$dF_3(y)/dy < 0, \quad 1 < y < (1+\beta_1+(\gamma+\alpha)\beta_2) \tag{E3}$$

Condition (E3) can be rewritten as

$$(y-1)f_3'(y) - f_3(y) < 0, \quad 1 < y < [1+\beta_1+(\gamma+\alpha)\beta_2] \tag{E4}$$

where

$$f_3(y) \triangleq X^{\mu+1}\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right] \tag{E5}$$

$$f_3'(y) = X^{\mu+1}\left[-1+\left(1+\beta_1+(\nu+\alpha)\beta_2-y\right)\frac{(\mu+1)\gamma_1}{y^2}\right] \tag{E6}$$

Substituting (E5)-(E6) into (E4) and collecting terms finally yields:

$$y^2\left[(\mu+1)\gamma_1+\beta_1+(\nu+\alpha)\beta_2\right]-y(\mu+1)\gamma_1\left[2+\beta_1+(\nu+\alpha)\beta_2\right]+$$
$$+(\mu+1)\gamma_1\left[1+\beta_1+(\nu+\alpha)\beta_2\right]>0 \tag{E7}$$

For (E7) to hold it suffices that

$$(\mu+1)^2\gamma_1^2\left[2+\beta_1+(\nu+\alpha)\beta_2\right]^2<$$
$$<4(\mu+1)\gamma_1\left[1+\beta_1+(\nu+\alpha)\beta_2\right]\left[(\mu+1)\gamma_1+\beta_1+(\nu+\alpha)\beta_2\right]$$

or

$$(\mu+1)\gamma_1\left[2+\beta_1+(\nu+\alpha)\beta_2\right]^2<$$
$$<4\left[1+\beta_1+(\nu+\alpha)\beta_2\right]\left[(\mu+1)\gamma_1+\beta_1+(\nu+\alpha)\beta_2\right] \tag{E8}$$

or

$$(\mu+1)\gamma_1\left[1+\beta_1+(\nu+\alpha)\beta_2\right]^2+(\mu+1)\gamma_1+2(\mu+1)\gamma_1\left[\beta_1+(\nu+\alpha)\beta_2+1\right]<$$
$$<4(\mu+1)\gamma_1\left[1+\beta_1+(\nu+\alpha)\beta_2\right]+4\left[1+\beta_1+(\nu+\alpha)\beta_2\right]\left[\beta_1+(\nu+\alpha)\beta_2\right]$$

or

$$(\mu+1)\gamma_1\left[1+\beta_1+(\nu+\alpha)\beta_2-1\right]^2<$$
$$<4\left[\beta_1+(\nu+\alpha)\beta_2\right]\left[1+\beta_1+(\nu+\alpha)\beta_2\right]$$

or

$$(\mu+1)\gamma_1\left[\beta_1+(\nu+\alpha)\beta_2\right]<4\left[1+\beta_1+(\nu+\alpha)\beta_2\right]$$

or

$$\gamma_1<\frac{4}{(\mu+1)}\left[1+\frac{1}{\beta_1+(\nu+\alpha)\beta_2}\right] \tag{E9}$$

A necessary and sufficient condition for the monotonicity of $F_1(y)$ in the interval $(1,\ 1+\beta_1)$ for all values of Da_2 is

$$\beta_1\gamma_1<4(1+\beta_1) \tag{E10}$$

A necessary and sufficient condition for the monotonicity of $F_2(y)$ in the interval $(1, 1+\alpha\beta_2)$ for all values of Da_2 is

$$\mu\gamma_1(\alpha\beta_2) < 4(1+\alpha\beta_2) \qquad \text{(E11)}$$

We will prove that condition (E9) is the most conservative of (E9)-(E11):

Suppose that (E9) is true. Then,

$$\gamma_1 < \frac{4}{(\mu+1)}\left[1+\frac{1}{\beta_1+(\nu+\alpha)\beta_2}\right] < \frac{4}{\mu}\left[1+\frac{1}{\beta_1+(\nu+\alpha)\beta_2}\right] <$$

$$< \frac{4}{\mu}\left[1+\frac{1}{\alpha\beta_2}\right] \qquad \text{(E12)}$$

Condition (E12) can be rewritten as

$$\mu\gamma_1(\alpha\beta_2) < 4(1+\alpha\beta_2)$$

which is in fact (E11). Therefore, (E9) implies (E11).

Again, suppose that (E9) holds. Then,

$$\gamma_1 < \frac{4}{(\mu+1)}\left[1+\frac{1}{\beta_1+(\nu+\alpha)\beta_2}\right] < 4\left[1+\frac{1}{\beta_1+(\nu+\alpha)\beta_2}\right] <$$

$$< 4\left[1+\frac{1}{\beta_1}\right] \qquad \text{(E13)}$$

(E13) can be rewritten as

$$\beta_1 \gamma_1 < 4(1+\beta_1)$$

which is in fact (E10). Therefore, (E9) implies (E10).

Consequently, (E9) is the most conservative of (E9)-(E11), and suffices for the monotonicity of the right-hand side of equ. (36) in the interval $(1,\ 1+\beta_1 + (\nu+\alpha)\beta_2)$.

APPENDIX F

Consider subproblem II. The steady state equation (10) becomes

$$\frac{1}{\beta_1} = F_1(y) + F_2(y) \tag{F1}$$

where

$$F_1(y) \triangleq \frac{\mathcal{D}a_1 / (\mathcal{D}a_1 + X^{-1})}{(y-1)} \tag{F2a}$$

$$F_2(y) \triangleq \frac{\alpha B \mathcal{D}a_2 / (\mathcal{D}a_2 + X^{-\mu})}{(y-1)} \tag{F2b}$$

Suppose that $\beta_1 > 0$, $B > 0$. Then, equ. (F1) will have a unique solution for all values of β_1 if $F_1(y)$ and $F_2(y)$ are monotonically decreasing functions of $y(>1)$. In other words, the conditions

$dF_1(y)/dy < 0, \quad y > 1$ ..... (F3)

$dF_2(y)/dy < 0, \quad y > 1$ ..... (F4)

are sufficient for uniqueness for all β_1 (>0) of equ. (F1).

Using (F2b), condition (F4) can be rewritten as

$$(y-1)\frac{\mathcal{D}a_2 X^{-\mu}\left(\frac{\mu\gamma_1}{y^2}\right)}{\left(\mathcal{D}a_2+X^{-\mu}\right)^2}-\frac{\mathcal{D}a_2}{\left(\mathcal{D}a_2+X^{-\mu}\right)}<0 \qquad \text{(F5)}$$

or

$$\mathcal{D}a_2 > g_2(y) \triangleq \frac{X^{-\mu}}{y^2}\left(-y^2+y\mu\gamma_1-\mu\gamma_1\right),\ 1<y \qquad \text{(F6)}$$

Similarly, condition (F3) can be rewritten as

$$\mathcal{D}a_1 > g_1(y) \triangleq \frac{X^{-1}}{y^2}\left(-y^2+y\gamma_1-\gamma_1\right),\ 1<y \qquad \text{(F7)}$$

(i) For subproblem II, we can always define the variables so that $\mu \geqslant 1$. From (F6)-(F7) it is clear that if

$$\mu\gamma_1 \leq 4 \qquad \text{(F8)}$$

then $g_1(y) < 0, g_2(y) < 0$, and, therefore, uniqueness is assured for all β_1 ($>$ 0) of equ. (F1).

(ii) Suppose that

$$\gamma_1 > 4$$

Then, for condition (F6) to hold it suffices that

$$\mathcal{D}a_2 > \max_{1<y} g_2(y) \qquad \text{(F9)}$$

Since

$$g_2'\left(\frac{\mu\gamma_1}{\mu\gamma_1-2}\right)=0 \tag{F10}$$

and

$$g_2''\left(\frac{\mu\gamma_1}{\mu\gamma_1-2}\right)=-\frac{\mu\gamma_1 X^{-\mu}}{y^4}(\mu\gamma_1-2)<0 \tag{F11}$$

it follows that $g_2(y)$ has a maximum at $y=\dfrac{\mu\gamma_1}{(\mu\gamma_1-2)}>1$

Thus, equ. (F9) becomes

$$\mathcal{D}a_2>\left(1-\frac{4}{\mu\gamma_1}\right)e^{-2} \tag{F12}$$

For condition (F7) to hold it suffices that

$$\mathcal{D}a_1>\max_{1<y} g_1(y) \tag{F13}$$

Following the same procedure as above we can prove that $g_1(y)$ has a maximum at

$$y=\frac{\gamma_1}{(\gamma_1-2)}>1$$

Consequently, condition (F13) becomes

$$\mathcal{D}a_1>\left(1-\frac{4}{\gamma_1}\right)e^{-2} \tag{F14}$$

Therefore, conditions (F12) and (F14) are sufficient for uniqueness for all values of β_1 ($>$ 0) of equ. (F1) when $\gamma_1 > 4$.

(iii) Suppose that

$$\gamma_1 \leq 4$$
$$\mu\gamma_1 > 4$$

Then, condition (F12) suffices for uniqueness for all values of β_1 ($>$ 0) of equ. (F1), because (F7) is satisfied.

APPENDIX G

Equ. (9) yields

$$(y-1)-\beta_1\frac{\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}=\beta_2\frac{\mathcal{D}a_2 X^{\mu}}{(1+\mathcal{D}a_2 X^{\mu})}\left[\alpha+\frac{\gamma\,\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}\right] \quad \text{(G1)}$$

Multiplying both sides of equ. (G1) by $(1+Da_2X^{\mu})$ yields

$$\frac{(y-1)(1+\mathcal{D}a_2 X^{\mu})(1+\mathcal{D}a_1 X)-\beta_1\mathcal{D}a_1 X(1+\mathcal{D}a_2 X^{\mu})}{(1+\mathcal{D}a_1 X)}=$$

$$=\beta_2\mathcal{D}a_2 X^{\mu}\left[\alpha+\frac{\gamma\,\mathcal{D}a_1 X}{(1+\mathcal{D}a_1 X)}\right]$$

Dividing numerator and denominator of the left-hand side by $(1+Da_2X^{\mu})$, the above equation becomes

$$\frac{(y-1)(1+\mathcal{D}a_1 X)-\beta_1\mathcal{D}a_1 X}{\mathcal{D}a_2\left[\frac{1+\mathcal{D}a_1 X}{1+\mathcal{D}a_2 X^{\mu}}\right]\frac{1}{X^{-\mu}}}=\beta_2\left[\alpha+\frac{\gamma}{\left(1+\frac{1}{\mathcal{D}a_1 X}\right)}\right]$$

Dividing both numerator and denominator of the left-hand side

by X yields

$$\frac{(y-1)(X^{-1}+Da_1)-\beta_1 Da_1}{Da_2\left[\dfrac{X^{-1}+Da_1}{X^{-\mu}+Da_2}\right]}=\beta_2\left[\alpha+\frac{\gamma}{\left(1+\dfrac{1}{Da_1 X}\right)}\right]$$

and

$$\frac{(y-1)X^{-1}-Da_1(1+\beta_1-y)}{Da_2\left[\dfrac{X^{-1}+Da_1}{X^{-\mu}+Da_2}\right]\left[\alpha+\dfrac{\gamma}{\left(1+\dfrac{X^{-1}}{Da_1}\right)}\right]}=\beta_2$$

Multiplying numerator and denominator of the left-hand side by X/Da_1 yields

$$\frac{\left[\dfrac{(y-1)}{Da_1}-X(1+\beta_1-y)\right]}{\sigma\left[\dfrac{X^{-1}+Da_1}{X^{-\mu}+Da_2}\right]\left[\alpha X+\dfrac{\gamma X}{\left(1+\dfrac{X^{-1}}{Da_1}\right)}\right]}=\beta_2$$

where

$$\sigma \triangleq \mathcal{D}a_2 / \mathcal{D}a_1$$

Assuming that $\beta_1 \neq 0$, and dividing both sides of the above equation by β_1 yields

$$(-B) \triangleq \left(-\frac{\beta_2}{\beta_1}\right) = \frac{-\left[\frac{(y-1)}{\mathcal{D}a_1} - X(1+\beta_1-y)\right]}{\sigma\beta_1 g(y)} \triangleq Z(y) \tag{G2}$$

where

$$g(y) \triangleq \left[\frac{X^{-1} + \mathcal{D}a_1}{X^{-\mu} + \mathcal{D}a_2}\right]\left[\alpha X + \frac{\gamma X}{\left(1 + \frac{X^{-1}}{\mathcal{D}a_1}\right)}\right] \tag{G2a}$$

Equ. (G2) is a different form of the steady state equation (9). The only asymptote occurs at y=0.

APPENDIX H

Fig.	γ_1	μ	β_1	β_2	$\mathcal{D}a_1$	ν	α
2a	20.0	1.2	0.6	0.2	0.04	0.0	1.0
	20.0	1.2	0.6	0.2	0.04	1.0	1.0
2b	20.0	1.2	0.4	0.2	.028	0.0	1.0
	20.0	1.2	0.4	0.2	.028	.01	1.0
2c	27.0	1.1	0.5	.05	.001	0.0	1.0
	20.0	1.2	0.4	0.2	.028	.00001	.10
	10.7	5.0	6.5	.09	.000275	1.0	0.0
2d	20.0	1.2	0.4	0.2	.028	.00001	2.0
	20.0	1.2	0.4	0.2	.028	0.0	10.
2e	10.7	5.0	6.5	.09	.000264	0.0	1.0
	10.7	5.0	6.5	.09	.000264	1.0	1.0
3a	17.0	1.0	0.8	0.5	.00511083	1.0	0.5
	17.0	1.2	0.8	0.3	"	0.0	1.0
3b	17.0	1.7	0.8	.02	"	.01	1.0
	17.0	2.0	0.8	1.0	"	0.0	.01
3c	17.0	2.0	0.8	1.0	"	10.	.01
	17.0	1.0	0.8	2.0	"	0.0	10.
3d	17.0	5.0	0.8	0.1	"	10.	0.2
3e	17.0	5.0	0.8	1.44	"	.00001	.10
3f	17.0	5.0	0.8	0.8	"	.00001	.10
4a	20.0	1.2	0.4	0.1	.04	0.0	1.0
	15.0	1.7	1.5	0.1	.01	.00001	1.0
	9.5	6.5	0.8	0.5	.06757	.10	0.0

Fig.	γ_1	μ	β_1	β_2	Da_1	ν	α
4b	20.0	1.2	0.4	0.02	0.04	0.0	1.0
	10.7	3.8	6.5	0.09	.001	.0001	1.0
	9.5	3.5	0.8	0.5	.06757	.01	0.0
4c	25.0	1.2	1.0	0.8	.01	0.0	1.0
	25.0	5.0	.875	0.8	.001	.00001	1.0
	9.5	3.5	0.8	0.5	.06757	1.0	0.0
4d	25.0	1.2	0.75	0.8	.001	1 .0	0.0
	28.0	1.0	1.0	1.0	.0001	10.0	0.0
4e	17.45	4.1	6.5	.09	.001	0.0	1.0
	10.7	4.1	6.5	.28	.001	.00001	1.0
4f	10.7	4.1	6.5	.277	.001	0.0	1.0
	10.7	5.0	6.5	.09	.001	.0001	1.0
4g	17.0	5.0	0.8	1.44	.00515	.00001	.10
4h	17.0	5.0	0.8	0.8	.0055	.00001	.10

	γ_1	μ	β_1	β_2	Da_2	ν	α
5a	10.0	4.0	.10	.30	1.0	1.0	0.0
	5.0	1.0	0.5	.40	100.	1.0	0.0
5b	10.0	4.0	0.2	.30	.0002	1.0	0.0
	25.0	1.2	1.0	.10	.01	.001	0.0
5c	10.0	4.0	0.1	.50	.0002	1.0	0.0
	8.0	4.0	0.1	.50	.0002	1.0	0.0
5d	9.5	3.5	0.8	.50	.0000002	1.0	0.0
5e	25.0	1.2	0.75	.80	.0000001	1.0	0.0
	28.0	1.0	1.0	1.0	.00000005	1.0	0.0

Fig.	γ_1	μ	β_1	β_2	Da_1	ν	α
6a	20.0	1.2	0.0	0.2	0.04	0.6	0.01
	10.7	5.0	0.0	.09	.001	.0001	0.50
6b	20.0	1.2	0.0	.2	.04	.6	2.0
	10.7	3.8	0.0	.09	.001	.0001	3.0
6c	25.0	1.2	0.0	.8	.01	1.0	.01
	25.0	1.2	0.0	.8	.01	1.0	0.0
6d	28.0	1.0	0.0	1.0	.00000005	1.0	1.0

	γ_1	μ	β_1	Da_1	Da_2	ν	α
7a	14.0	1.0	0.5	0.10	10.0	100.	1.0
	8.0	1.0	0.7	0.50	.001	0.0	1.0
	15.0	2.0	0.1	5.0	100.	.10	0.0
7b	20.	1.2	0.6	.04	.71	1.0	1.0
	14.0	1.0	0.5	.10	10.	0.0	1.0
	20.	1.2	0.6	.04	.71	.10	0.0
7c	20.	1.2	0.4	.04	.952	.01	1.0
	20.0	1.2	0.4	.04	.952	0.0	1.0
	20.0	1.2	0.4	.04	.952	0.10	0.0
7e	20.0	1.2	0.4	.028	.909	10.	1.0
	20.0	1.2	0.4	.028	.909	0.0	1.0
	10.0	4.0	0.10	.50	.0002	10.	0.0
7d	17.0	1.7	.8	.00511083	.50	.01	1.0
	17.0	1.7	.8	"	2.0	0.0	1.0
	17.0	2.0	.8	"	.005	10.	0.0

Fig.	γ_1	μ	β_1	$\mathcal{D}a_1$	$\mathcal{D}a_2$	ν	α
7f	20.0	1.2	0.60	0.04	.71	500.	0.0
7g	20.0	1.2	0.40	0.04	.952	1.0	0.0
	20.0	1.2	0.40	0.04	.952	.001	0.0
7h	20.0	1.0	0.10	0.05	100.	.50	0.0
7i	20.0	1.2	0.40	.04	.00001	1.0	1.0
	20.0	1.2	0.40	.04	.00001	0.0	1.0
	9.50	3.5	0.80	.06757	.0000004	1.0	0.0
7j	17.45	4.1	6.5	.001	.0027	1.0	1.0
7k	28.0	1.0	0.10	.00000005	.00002	1.0	1.0
7l	20.0	1.2	0.0	.04	.952	.10	1.0
	14.0	1.0	0.0	.10	10.0	100.	0.0
7m	20.0	1.2	0.0	.04	.00001	100.	1.0
	17.45	4.1	0.0	.001	.0027	.01	0.0
7n	28.0	1.0	0.0	.00000005	.00002	1.0	1.0

APPENDIX I

Consider equ. (20)

$$(1+\alpha\beta_2-y)+\mathcal{D}a_1 X\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]=0$$

which can be rewritten as

$$G(y)\triangleq\frac{X\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]}{\left[y-(1+\alpha\beta_2)\right]}=\frac{1}{\mathcal{D}a_1} \qquad \text{(I1)}$$

A necessary and sufficient condition for uniqueness for all Da_1 of equ. (I1) is

$$dG(y)/dy < 0, \qquad (1+\alpha\beta_2) < y < (1+\beta_1+(\nu+\alpha)\beta_2) \qquad \text{(I2)}$$

Using (I1), (I2) can be rewritten as

$$\left[y-(1+\alpha\beta_2)\right]X\left\{-1+\left(\frac{\gamma_1}{y^2}\right)\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]\right\}-$$
$$-X\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]<0 \qquad \text{(I3)}$$

or

$$-(\beta_1+\nu\beta_2+\gamma_1)y^2+y\gamma_1\left\{\left[1+\beta_1+(\nu+\alpha)\beta_2\right]+(1+\alpha\beta_2)\right\}-$$
$$-\gamma_1(1+\alpha\beta_2)\left[1+\beta_1+(\nu+\alpha)\beta_2\right]<0 \qquad \text{(I4)}$$

For (I4) to hold, it suffices that

$$\gamma_1^2\left\{\left[1+\beta_1+(\nu+\alpha)\beta_2\right]+(1+\alpha\beta_2)\right\}^2 <$$
$$< 4\gamma_1(1+\alpha\beta_2)(\beta_1+\nu\beta_2+\gamma_1)\left[1+\beta_1+(\nu+\alpha)\beta_2\right]$$

or

$$\gamma_1(\beta_1+\nu\beta_2) < 4(1+\alpha\beta_2)\left[1+\beta_1+(\nu+\alpha)\beta_2\right] \qquad \text{(I5)}$$

A sufficient condition for multiplicity for some Da_1 values of equ. (I1) is:

$dG(y)/dy > 0$ for some y in $(1+\alpha\beta_2) < y < y^* < (1+\beta_1+(\nu+\alpha)\beta_2)$ (I6)

where y* is the largest root of equ.(20).

Condition (I6) can be rewritten as

$$-(\beta_1+\nu\beta_2+\gamma_1)y^2+y\gamma_1\left\{\left[1+\beta_1+(\nu+\alpha)\beta_2\right]+(1+\alpha\beta_2)\right\}-$$
$$-\gamma_1(1+\alpha\beta_2)\left[1+\beta_1+(\nu+\alpha)\beta_2\right] > 0 \qquad \text{(I7)}$$

for some values of y in $(1+\alpha\beta_2) < y < y^*$.

For (I7) to hold, it suffices that

$$\gamma_1(\beta_1+\nu\beta_2) > 4(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2] \tag{I8a}$$

$$\rho_1 < y^* \tag{I8b}$$

where ρ_1 is the smallest root of the equation

$$-(\beta_1+\nu\beta_2+\gamma_1)y^2+y\gamma_1\{[1+\beta_1+(\nu+\alpha)\beta_2]+(1+\alpha\beta_2)\}-$$
$$-\gamma_1(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2]=0 \tag{I9}$$

Condition (I8a) assures that equ. (I9) has two real and unequal roots, while (I8b) assures that (I7) will hold for values of y in the interval (ρ_1 , y*).
Observe that $(1+\alpha\beta_2) < \rho_1 < \rho_2 < (1+\beta_1+(\nu+\alpha)\beta_2)$. This concludes the proof for Lemma 3b6.

Clearly, uniqueness is also assured if

$$\gamma_1(\beta_1+\nu\beta_2) > 4(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2] \tag{I10}$$

$$\rho_1 < y^* \tag{I11}$$

and either

$$1/\mathcal{D}a_1 > \max_{(1+\alpha\beta_2)<y<y^*} G(y) \tag{I12}$$

or

$$1/\mathcal{D}a_1 < \min_{(1+\alpha\beta_2)<y<y^*} G(y) \tag{I13}$$

APPENDIX J

Lemma J: Suppose that $\beta_1 \geqslant 0,\ \beta_2 > 0$. A sufficient condition for multiplicity for some Da_2 values of equ. (21) is

$dF(y)/dy > 0$ for some y in the interval

$$1 \leqslant y^{**} < y < y^{*} < (1+\beta_1 + (\nu+\alpha)\beta_2). \tag{J1}$$

Condition (J1) can be rewritten as

$$\beta_2 y^2 + \mu\gamma_1 (y-1)\,\theta(y)\left\{(y-1) - \left[\alpha\beta_2 + h_1(y) + h_2(y)\right]\right\} + \\ + \mu\gamma_1\beta_1 M(y) < 0 \tag{J2}$$

for some y in $y^{**} < y < y^{*}$.

For (J2) to hold it suffices that

$$\beta_2 y^2 + \mu\gamma_1 (y-1)\,\underline{\theta}\left\{(y-1) - \left[\alpha\beta_2 + \underline{h_1} + \underline{h_2}\right]\right\} + \mu\gamma_1\beta_1\overline{M} < 0 \tag{J3}$$

for some y in $y^{**} < y < y^{*}$.

(J3) can be rewritten as

$$(\beta_2 + \mu\gamma_1\underline{\theta})\,y^2 - \mu\gamma_1\underline{\theta}\,(2 + \alpha\beta_2 + \underline{h_1} + \underline{h_2})\,y + \\ + \mu\gamma_1\left[\underline{\theta}\,(1 + \alpha\beta_2 + \underline{h_1} + \underline{h_2}) + \beta_1\overline{M}\right] < 0 \tag{J4}$$

for some y in $y^{**} < y < y^{*}$.

For (J4) to hold it suffices that

$$\mu\gamma_1 \underline{\theta}^2 (2+\alpha\beta_2+\underline{h_1}+\underline{h_2})^2 > 4(\beta_2+\mu\gamma_1\underline{\theta}) * \\ * \left[\underline{\theta}(1+\alpha\beta_2+\underline{h_1}+\underline{h_2})+\beta_1\overline{M}\right] \tag{J5a}$$

and either

$$\left.\begin{array}{l} y^{**} < x_1 < y^* \\ \text{or} \\ x_1 < y^{**} < x_2 < y^* \end{array}\right\} \tag{J5b}$$

where x_1 x_2 are roots of (J4)=0.

In (J5a) we could substitute

$$\underline{\theta} \triangleq \min_{y^{**}<y<y^*} \theta(y) = \theta(y^*) > \theta(1+\delta) \tag{J6a}$$

$$\underline{h_1} \triangleq \min_{y^{**}<y<y^*} h_1(y) = h_1(y^{**}) > h_1(1) = \frac{(2\beta_1+\nu\beta_2)}{\left(1+\frac{1}{\mathcal{D}a_1}\right)} \tag{J6b}$$

$$\underline{h_2} \triangleq \min_{y^{**}<y<y^*} h_2(y) > \frac{(\nu\beta_2/\mu)}{\left(2+\frac{1}{\mathcal{D}a_1}+\mathcal{D}a_1 X(1+\delta)\right)} \tag{J6c}$$

$$\left.\overline{M} \triangleq \max_{y^{**}<y<y^*} M(y) = M(y^*) < M(1+\delta) \quad \text{if } \mu \geqslant 1\right\} \tag{J6d}$$

When $\mu < 1$, however, then from (24d) it follows that

$$M(y) < \frac{[\beta_1 + (\nu+\alpha)\beta_2]\,\mathcal{D}a_1^2 X^2}{(1+\mathcal{D}a_1 X)[\alpha + (\nu+\alpha)\mathcal{D}a_1 X]} <$$

$$< \frac{[\beta_1 + (\nu+\alpha)\beta_2]}{(\nu+\alpha) + \dfrac{(\nu+2\alpha)}{\mathcal{D}a_1 X(1+\delta)} + \dfrac{\alpha}{(\mathcal{D}a_1 X(1+\delta))^2}} \triangleq \overline{M} \qquad \text{(J6e)}$$

Clearly, conditions (J5b) are impractical because y**, y* must be determined numerically.

APPENDIX K

Fig.	γ_1	μ	β_1	β_2	Da_1	ν	α
8a	15.0	1.0	-5.0	6.0	100.0	500.0	1.0
	5.0	1.0	-0.5	1.0	.001	10.0	1.0
	10.	1.0	-1.0	0.2	.01	10.0	1.0
	4.0	0.8	-.01	5.0	15.	.01	0.0
	5.0	1.0	-.05	1.0	.001	0.0	1.0
8b	5.0	1.0	-0.5	1.0	.001	100.	1.0
	14.	1.0	-0.2	10.	.0001	.00001	1.0
	10.0	0.7	-1.0	0.2	.10	50.	1.0
8c	20.0	1.0	-0.1	0.02	.001	100.	0.0
	18.0	0.1	-0.8	1.0	.00001	100.	0.0
8d	5.0	1.0	0.5	-2.	1.0	0.0	1.0
	15.	1.5	2.0	-1.0	.10	5.0	1.0
	6.0	0.6	0.5	-1.0	.01	0.0	1.0
8e	5.0	1.0	0.5	-0.8	.001	0.0	1.0
	5.0	1.0	0.5	-0.3	.0001	1.0	1.0
	5.0	2.0	0.1	-5.0	85.0	0.10	0.0
	8.0	0.6	0.1	-5.0	100.	0.10	0.0
8f	3.0	2.0	1.5	-2.0	200,000	0.10	1.0
	3.0	0.9	1.5	-2.0	200,000	0.10	1.0
8g	20.0	1.0	0.4	-0.2	0.06	5.0	0.0
	20.0	0.8	0.4	-0.2	0.06	5.0	0.0

Fig.	γ_1	μ	β_1	β_2	$\mathcal{D}a_1$	γ	α
8h	15.0	1.5	1.5	-2.0	0.01	0.0	1.0
	15.0	1.0	6.0	-2.0	.0001	0.0	3.5
	15.0	0.8	1.5	-2.0	.01	0.0	1.0
8i	15.0	1.0	1.0	-0.5	.01	10.0	1.0
	10.0	1.5	2.0	-0.1	.01	50.0	1.0
	16.0	2.0	0.8	-.008	.01	200.	0.0
	15.0	0.3	1.0	-0.5	.01	100.	1.0

APPENDIX L

Consider equ. (115)

$$(1+\alpha\beta_2-y)+\mathcal{D}a_1 X\left[1+\beta_1+(\gamma+\alpha)\beta_2-y\right]=0 \tag{L1}$$

Equ. (L1) can be rewritten as

$$G(y)\triangleq\frac{X\left[1+\beta_1+(\gamma+\alpha)\beta_2-y\right]}{\left[y-(1+\alpha\beta_2)\right]}=\frac{1}{\mathcal{D}a_1} \tag{L2}$$

Since $\beta_1<0$, $\beta_2>0$, and $\left[1+(\gamma+\alpha)B\right]\leq 0$, it follows that

$$\left[\beta_1+(\gamma+\alpha)\beta_2\right]\geqslant 0 \tag{L3}$$

If

$$(\beta_1+\gamma\beta_2)>0 \tag{L4}$$

then $$0<(1+\alpha\beta_2)<\left[1+\beta_1+(\gamma+\alpha)\beta_2\right] \tag{L4a}$$

If

$$(\beta_1+\gamma\beta_2)<0 \tag{L5}$$

then $$0<\left[1+\beta_1+(\gamma+\alpha)\beta_2\right]<(1+\alpha\beta_2) \tag{L5a}$$

If (L4) holds, then a necessary and sufficient condition for uniqueness for all Da_1 of equ. (L2) is

$$dG(y)/dy < 0, \text{ where } (1+\alpha\beta_2) < y < (1+\beta_1+(\nu+\alpha)\beta_2) \tag{L6}$$

As shown in Appendix I, (L6) yields

$$\gamma_1(\beta_1+\nu\beta_2) < 4(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2] \tag{L7}$$

If (L5) holds, then a necessary and sufficient condition for uniqueness for all Da_1 of equ. (L2) is

$$dG(y)/dy > 0, \ (1+\beta_1+(\nu+\alpha)\beta_2) < y < (1+\alpha\beta_2) \tag{L8}$$

As shown in Appendix I, (L8) can be rewritten as

$$-(\beta_1+\nu\beta_2+\gamma_1)y^2+y\gamma_1\{[1+\beta_1+(\nu+\alpha)\beta_2]+(1+\alpha\beta_2)\}- \\ -\gamma_1(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2] > 0 \tag{L9}$$

For (L9) to hold it suffices that

$$(\beta_1+\nu\beta_2+\gamma_1) > 0 \tag{L10}$$

$$\gamma_1(\beta_1+\nu\beta_2) < 4(1+\alpha\beta_2)[1+\beta_1+(\nu+\alpha)\beta_2] \tag{L11}$$

$$\rho_1 < [1+\beta_1+(\nu+\alpha)\beta_2] < (1+\alpha\beta_2) < \rho_2 \tag{L12}$$

where ρ_1, ρ_2, are roots of (L9)=0.

Observe that (L11) is automatically satisfied since $(\beta_1+\nu\beta_2) < 0$.

APPENDIX M

Consider condition (68b). Suppose that Da_1 is such that equ. (66) has only one root, y^{**}, where $1 < y^{**} < (1+\beta_1)$. Let y^* denote the smallest root of equ. (67) where either $(1+\alpha\beta_2) < y^* < (1+\delta)$ or $(1+\delta) < y^* < (1+\alpha\beta_2)$.

Since $[1+(\gamma+\alpha)B] \leq 0$, it follows from (64) that $F(1) \geq 0$. Depending on the sign of the quantity $(\beta_1+\gamma\beta_2)$ and the position of zero on the dimensionless temperature axis, the following arrangements are possible:

$$0<(1+\alpha\beta_2)<y^*<[1+\beta_1+(\gamma+\alpha)\beta_2]<1<y^{**}<(1+\beta_1) \quad \text{(M1)}$$

$$(1+\alpha\beta_2)<0<y^*<[1+\beta_1+(\gamma+\alpha)\beta_2]<1<y^{**}<(1+\beta_1) \quad \text{(M2)}$$

$$(1+\alpha\beta_2)<[1+\beta_1+(\gamma+\alpha)\beta_2]<0<1<y^{**}<(1+\beta_1) \quad \text{(M3)}$$

$$0<[1+\beta_1+(\gamma+\alpha)\beta_2]<y^*<(1+\alpha\beta_2)<1<y^{**}<(1+\beta_1) \quad \text{(M4)}$$

$$[1+\beta_1+(\gamma+\alpha)\beta_2]<0<y^*<(1+\alpha\beta_2)<1<y^{**}<(1+\beta_1) \quad \text{(M5)}$$

$$[1+\beta_1+(\gamma+\alpha)\beta_2]<(1+\alpha\beta_2)<0<1<y^{**}<(1+\beta_1) \quad \text{(M6)}$$

$$0<y^*=(1+\alpha\beta_2)<1<y^{**}<(1+\beta_1) \quad \text{(M7)}$$

$$(1+\alpha\beta_2)<0<1<y^{**}<(1+\beta_1) \quad \text{(M8)}$$

From (M1)-(M8), we see that in (68b) we must substitute:

$$\overset{+}{y}=\begin{cases} y^* \text{ for arrangements (M1), (M4), (M5)} \\ 0 \text{ for arrangements (M2), (M3), (M6), (M8)} \\ (1+\alpha\beta_2) \text{ for arrangement (M7)} \end{cases} \qquad \text{(M9)}$$

Observe that when equ. (67) has two roots, then we must substitute $\overset{+}{y}=0$ instead of $\overset{+}{y}=y^*$ for the arrangements (M1), (M4) and (M5).

APPENDIX N

Consider the case where $\beta_1 > 0$, $\beta_2 < 0$, and $\mu < 1$. From (70d) it follows that

$$M(y) < \frac{(\mu-1)\,\alpha\beta_2\,\mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)[\alpha+(r+\alpha)\mathcal{D}a_1 X]} =$$

$$= \frac{\frac{(\mu-1)}{\mu}\,\alpha\beta_2}{\left[(r+2\alpha)+(r+\alpha)\mathcal{D}a_1 X+\frac{\alpha}{\mathcal{D}a_1 X}\right]} < \frac{(\mu-1)\,\alpha\beta_2}{\mu(r+2\alpha)} \triangleq \overline{M}$$

From (73a), (70d) and (70a) it follows that

$$M^*(y) \triangleq \frac{\mathcal{D}a_1^2 X^2[\beta_1+(r+\alpha)\beta_2]}{(1+\mathcal{D}a_1 X)^2} + \frac{(\mu-1)\,\alpha\beta_2\,\mathcal{D}a_1 X}{\mu(1+\mathcal{D}a_1 X)^2}$$

or

$$M^*(y) \triangleq [\beta_1+(r+\alpha)\beta_2]\left(\frac{1}{1+\frac{1}{\mathcal{D}a_1 X}}\right)^2 + \frac{\frac{(\mu-1)}{\mu}\,\alpha\beta_2}{\left(2+\mathcal{D}a_1 X+\frac{1}{\mathcal{D}a_1 X}\right)}$$

Since $[1+(\nu+\alpha)B] \leq 0$ and $\beta_1 < 0$, $\beta_2 > 0$, it follows that $[\beta_1+(\nu+\alpha)\beta_2] \geqslant 0$. Clearly,

$$M^*(y) \leq [\beta_1+(\nu+\alpha)\beta_2] + \frac{\frac{(\mu-1)}{\mu}\alpha\beta_2}{\left(2+\mathcal{D}a_1\bar{X}+\frac{1}{\mathcal{D}a_1\bar{X}}\right)}$$

Suppose that $\mu \geqslant 1$. Since $\beta_1 < 0$, $\beta_2 > 0$, we have that

$$0 \leq \frac{\frac{(\mu-1)}{\mu}\alpha\beta_2}{\left(2+\mathcal{D}a_1\bar{X}+\frac{1}{\mathcal{D}a_1\bar{X}}\right)} < \frac{(\mu-1)\alpha\beta_2}{2\mu}$$

Consequently,

$$M^*(y) \leq [\beta_1+(\nu+\alpha)\beta_2] + \frac{(\mu-1)\alpha\beta_2}{2\mu} \triangleq \overline{M^*}$$

When, however, $\mu < 1$, then since $\beta_1 < 0$, $\beta_2 > 0$, it follows that

$$\frac{\frac{(\mu-1)}{\mu}\alpha\beta_2}{\left(2+\mathcal{D}a_1\bar{X}+\frac{1}{\mathcal{D}a_1\bar{X}}\right)} < 0$$

Consequently, when $\mu < 1$ and $\beta_1 < 0$, $\beta_2 > 0$, then

$$M^*(y) < \left[\beta_1 + (\nu + \alpha)\beta_2\right] + \frac{\frac{(\mu-1)}{\mu}\alpha\beta_2}{\left(2 + \mathcal{D}a_1 \bar{X} + \frac{1}{\mathcal{D}a_1 \bar{X}}\right)} <$$

$$< \left[\beta_1 + (\nu + \alpha)\beta_2\right] \triangleq \overline{M^*}$$

APPENDIX O

Fig.	γ_1	μ	β_1	β_2	$\mathcal{D}a_2$	γ	α
9a	5.0	2.0	1.0	-0.5	.00001	2.0	0.0
	6.0	3.0	3.0	-1.0	1.0	2.0	0.0
9b	14.	1.0	0.5	-0.3	.001	.0001	0.0
	10.	3.0	1.0	-0.5	.0001	2.0	0.0
	11.	1.0	4.0	-0.5	.0001	8.0	0.0
9c	5.0	2.0	-1.1	0.9	10.	0.10	0.0
	15.	1.0	-3.5	0.4	0.10	0.70	0.0
9d	5.0	1.0	-0.5	0.9	100.	0.10	0.0
	15.	1.0	-0.3	0.4	0.01	0.70	0.0
9e	8.0	2.0	-0.5	0.9	1000.	0.30	0.0
9f	5.0	3.0	-0.5	0.9	500.	0.5	0.0
10a	10.	2.0	2.0	-0.5	0.01	1.0	1.0
	5.0	2.0	1.0	-.10	0.10	0.0	1.0
10b	10.0	2.0	2.0	-0.5	10.0	0.10	1.0
	20.0	1.0	0.5	-.01	10.0	0.0	1.0
10c	10.	1.0	-2.0	0.2	.001	0.0	1.0
	10.	2.0	-2.0	0.2	1.0	1.0	1.0
10d	10.	2.0	-0.5	0.3	.001	.0001	1.0
10e	5.0	1.0	-1.0	0.5	8,000	.0001	1.0
10f	17.0	1.0	-2.0	0.8	0.01	1.0	1.0
	17.0	1.0	-2.0	0.8	0.01	0.0	1.0

APPENDIX P

Consider equ. (114) which can be rewritten as

$$\frac{1}{\mathcal{D}a_2} = \frac{X^{\mu}\left[1+\beta_1+(\nu+\alpha)\beta_2-y\right]}{\left[y-(1+\beta_1)\right]} \triangleq G(y) \qquad \text{(P1)}$$

A necessary and sufficient condition for uniqueness for all Da_2 of equ. (P1) is

$$dG(y)/dy > 0, \text{ where } (1+\beta_1+(\nu+\alpha)\beta_2) < y < (1+\beta_1) \qquad \text{(P2)}$$

Condition (P2) yields

$$-y^2\left[(\nu+\alpha)\beta_2+\mu\gamma_1\right]+y\mu\gamma_1\left\{\left[1+\beta_1+(\nu+\alpha)\beta_2\right]+(1+\beta_1)\right\}-$$
$$-\mu\gamma_1(1+\beta_1)\left[1+\beta_1+(\nu+\alpha)\beta_2\right] > 0 \qquad \text{(P3)}$$

For (P3) to hold it suffices that

$$\left[(\nu+\alpha)\beta_2+\mu\gamma_1\right] > 0 \qquad \text{(P4)}$$

$$\mu\gamma_1(\nu+\alpha)\beta_2 < 4(1+\beta_1)\left[1+\beta_1+(\nu+\alpha)\beta_2\right] \qquad \text{(P5)}$$

$$\rho_1 < \left[1+\beta_1+(\nu+\alpha)\beta_2\right] < (1+\beta_1) < \rho_2 \qquad \text{(P6)}$$

where ρ_1, ρ_2, are roots of (P3)=0. Observe that (P5) is automatically satisfied since $\beta_2 < 0$. Instead of (P4)-(P6) we could require that

$$\left[(\nu+\alpha)\beta_2+\mu\gamma_1\right]<0 \tag{P7}$$

and either that

$$(1+\beta_1)<\rho_1 \tag{P8a}$$

or

$$\rho_2<\left[1+\beta_1+(\nu+\alpha)\beta_2\right] \tag{P8b}$$

APPENDIX Q

Consider condition (119b). Let Da_2 be such that equ. (117) has only one root, y**, where $1<y^{**}<(1+\alpha\beta_2)$. Let y* be the smallest root of equ. (118) where y* lies between $(1+\beta_1)$ and $(1+\beta_1+(\nu+\alpha)\beta_2)$.

From (65) it follows that $\Phi(1)>0$. Depending on the position of zero on the dimensionless temperature axis, the following arrangements are possible:

$$0<(1+\beta_1)<y^{*}<\left[1+\beta_1+(\nu+\alpha)\beta_2\right]<1<y^{**}<(1+\alpha\beta_2) \tag{Q1}$$

$$(1+\beta_1)<0<\left[1+\beta_1+(\nu+\alpha)\beta_2\right]<1<y^{**}<(1+\alpha\beta_2) \tag{Q2}$$

$$(1+\beta_1)<\left[1+\beta_1+(\nu+\alpha)\beta_2\right]<0<1<y^{**}<(1+\alpha\beta_2) \tag{Q3}$$

From (Q1)-(Q3) it follows that in (119b) we must substitute:

$$\overset{+}{y}=\begin{cases} y^* \text{ for arrangement (Q1)} \\ \\ 0 \text{ for arrangements (Q2), (Q3)} \end{cases}$$

Observe that if equ. (118) has two roots, then we must use $\overset{+}{y}=0$ instead of $\overset{+}{y}=y^*$ for arrangement (Q1).

APPENDIX R

Lemma R1: Suppose that $\beta_1 \geq 0,\ \beta_2 > 0$. Let Da_2 be such that the equation

$$F_D \triangleq \left[(y-1) - \mathcal{D}a_2 X^{\mu}(1+\alpha\beta_2 - y)\right] = 0 \qquad \text{(R1a)}$$

has only one root, $1 < y^{**} < (1+\alpha\beta_2)$, and let

$$(1+\beta_1) < y^* < (1+\beta_1 + (\gamma+\alpha)\beta_2)$$

denote the largest root of the equation

$$F_N \triangleq \left\{(1+\beta_1 - y) + \mathcal{D}a_2 X^{\mu}[1+\beta_1+(\gamma+\alpha)\beta_2 - y]\right. = 0 \qquad \text{(R1b)}$$

THEN, a necessary and sufficient condition for uniqueness for all Da_1 of the steady state equation

$$\frac{1}{\mathcal{D}a_1} = \frac{X F_N}{F_D} \triangleq \Phi(y) \qquad \text{(R2)}$$

is

$$\frac{d\Phi(y)}{dy} < 0 \quad \text{, where } y^{**} < y < y^* \qquad \text{(R3)}$$

Condition (R3) yields

$$-\beta_1 y^2+\gamma_1(y-1)\Theta(y)\left\{(1+\beta_1-y)+\left[h_1(y)+h_2(y)\right]\right\}-$$
$$-\gamma_1\alpha\beta_2\left[M_1(y)+M_2(y)\right]<0\,,\ y^{**}<y<y^{*} \tag{R4}$$

where

$$\Theta(y)\triangleq\frac{(1+\mathcal{D}a_2\mathbb{X}^{\mu})}{\left[1+(1+\gamma B)\mathcal{D}a_2\mathbb{X}^{\mu}\right]}>0 \tag{R5a}$$

$$h_1(y)\triangleq\frac{2\alpha\beta_2\mathcal{D}a_2\mathbb{X}^{\mu}}{(1+\mathcal{D}a_2\mathbb{X}^{\mu})}>0 \tag{R5b}$$

$$h_2(y)\triangleq\frac{\gamma\beta_2\mathcal{D}a_2\mathbb{X}^{\mu}\left[\mu+(1+\mathcal{D}a_2\mathbb{X}^{\mu})\right]}{(1+\mathcal{D}a_2\mathbb{X}^{\mu})^2}>0 \tag{R5c}$$

$$M_1(y)\triangleq\frac{-(\mu-1)\beta_1\mathcal{D}a_2\mathbb{X}^{\mu}}{(1+\mathcal{D}a_2\mathbb{X}^{\mu})\left[1+(1+\gamma B)\mathcal{D}a_2\mathbb{X}^{\mu}\right]}=$$
$$=\begin{Bmatrix}\leq 0\ , & \mu\geqslant 1\\ >0\ , & \mu<1\end{Bmatrix} \tag{R5d}$$

$$M_2(y) \triangleq \frac{[\beta_1+(\nu+\alpha)\beta_2]\,(\mathcal{D}a_2 X^{\mu})^2}{(1+\mathcal{D}a_2 X^{\mu})[1+(1+\nu B)\mathcal{D}a_2 X^{\mu}]} > 0 \qquad \text{(R5e)}$$

Condition (R4) can be rewritten as

$$\beta_1 y^2+\gamma_1(y-1)\Theta(y)\left\{(y-1)-[\beta_1+h_1(y)+h_2(y)]\right\}+$$

$$+\gamma_1\alpha\beta_2[M_1(y)+M_2(y)]>0 \qquad \text{(R6)}$$

$$y^{**}<y<y^{*}$$

OR

$$\frac{\beta_1}{\Theta(y)}y^2+\gamma_1(y-1)\left\{(y-1)-[\beta_1+h_1(y)+h_2(y)]\right\}+$$

$$+\gamma_1\alpha\beta_2 M^{*}(y)>0,\ y^{**}<y<y^{*} \qquad \text{(R7)}$$

where

$$M^{*}(y) \triangleq \frac{M_1(y)+M_2(y)}{\Theta(y)} \qquad \text{(R8)}$$

For (R7) to hold it suffices that

$$\frac{\beta_1}{\bar{\theta}} y^2 + \gamma_1 (y-1)\left\{(y-1) - \left[\beta_1 + \bar{h}_1 + \bar{h}_2\right]\right\} + \\ + \gamma_1 \alpha \beta_2 \underline{M}^* > 0, \; y^{**} < y < y^* \qquad \text{(R9)}$$

Condition (R9) can be rewritten as

$$y^2(\beta_1 + \gamma_1 \bar{\theta}) - y \gamma_1 \bar{\theta}\left[2 + \beta_1 + \bar{h}_1 + \bar{h}_2\right] + \\ + \gamma_1 \bar{\theta}\left(1 + \beta_1 + \alpha \beta_2 \underline{M}^* + \bar{h}_1 + \bar{h}_2\right) > 0 \qquad \text{(R10)} \\ y^{**} < y < y^*$$

For (R10) to hold it suffices that

$$\gamma_1 \bar{\theta}\left(2 + \beta_1 + \bar{h}_1 + \bar{h}_2\right)^2 < 4(\beta_1 + \gamma_1 \bar{\theta}) * \\ * \left(1 + \beta_1 + \alpha \beta_2 \underline{M}^* + \bar{h}_1 + \bar{h}_2\right) \qquad \text{(R11)}$$

Next, we will consider:

(1) Subproblem I(i) ($\nu \neq 0, \alpha \neq 0$)

(2) Subproblem II ($\nu \equiv 0, \alpha \neq 0$)

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1. Subproblem I(i) ($\nu \neq 0, \alpha \neq 0$)

In (R11) the following substitutions can be made:

$$\overline{\Theta} = \Theta(1) = \frac{(1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]} < 1 \tag{R12a}$$

because $\Theta'(y) < 0$.

$$\overline{h}_1 = 2\alpha\beta_2 > h_1(y) \triangleq \frac{2\alpha\beta_2}{\left(1+\frac{1}{\mathcal{D}a_2 X^{\mu}}\right)} \tag{R12b}$$

$$\overline{h}_2 = \nu\beta_2\left(1+\frac{\mu}{4}\right) > h_2(y) \tag{R12c}$$

$$\underline{M}^* \triangleq M^*(1) = \frac{[\beta_1+(\nu+\alpha)\beta_2]\mathcal{D}a_2^2 - (\mu-1)\beta_1\mathcal{D}a_2}{(1+\mathcal{D}a_2)^2} \tag{R12d}$$

Making the above substitutions (R11) yields:

$$\frac{\gamma_1 (1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]}\left[2+\beta_1+2\alpha\beta_2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right]^2 <$$

$$< 4\left(\beta_1+\frac{\gamma_1(1+\mathcal{D}a_2)}{[1+(1+\nu B)\mathcal{D}a_2]}\right)*$$

$$*\left[1+\beta_1+\alpha\beta_2\underline{M}^*+2\alpha\beta_2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right] \qquad \text{(R12e)}$$

If we use $\overline{\Theta}=1$ instead, then (R12e) further simplifies to

$$\gamma_1\left[2+\beta_1+2\alpha\beta_2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right]^2 < 4(\beta_1+\gamma_1)*$$

$$*\left[1+\beta_1+\alpha\beta_2(\underline{M}^*+2)+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right] \qquad \text{(R12f)}$$

Observe that for $\beta_2=0$, (R12e) degenerates to that of a single chemical reaction

$$\gamma_1(2+\beta_1)^2<4(\beta_1+\gamma_1)(1+\beta_1) \Rightarrow \beta_1\gamma_1<4(1+\beta_1)$$

2. Subproblem II ($\gamma \equiv 0$, $\alpha \neq 0$)

Since $\gamma \equiv 0$, it follows from (R5a), (R5c), that

$$\Theta(y) = 1$$
$$h_2(y) = 0$$

Consequently, condition (R11) becomes

$$\gamma_1(2+\beta_1+\bar{h}_1)^2 < 4(\beta_1+\gamma_1)(1+\beta_1+\alpha\beta_2\underline{M}^*+\bar{h}_1) \tag{R13}$$

Substituting (R12b) into (R13) yields

$$\gamma_1(2+\beta_1+2\alpha\beta_2)^2 < 4(\beta_1+\gamma_1)[1+\beta_1+\alpha\beta_2\underline{M}^*+2\alpha\beta_2] \tag{R14}$$

OR

$$\gamma_1[2(1+\alpha\beta_2)+\beta_1]^2 < 4(\beta_1+\gamma_1)[1+\beta_1+\alpha\beta_2(\underline{M}^*+2)] \tag{R15}$$

Substituting (R12d) (with $\gamma \equiv 0$) into (R15) yields

$$\gamma_1[2(1+\alpha\beta_2)+\beta_1]^2 < 4(\beta_1+\gamma_1) *$$
$$* \left\{1+\beta_1+\alpha\beta_2\left[2+(\beta_1+\alpha\beta_2)\left(\frac{\mathcal{D}a_2}{1+\mathcal{D}a_2}\right)^2-\frac{(\mu-1)\beta_1\mathcal{D}a_2}{(1+\mathcal{D}a_2)^2}\right]\right\} \tag{R16}$$

When μ =1, (R16) simplifies even further. Observe that for β_2 =0, (R15) degenerates to that of a single chemical reaction occuring in a lumped parameter system:

$$\beta_1\gamma_1 < 4(1+\beta_1)$$

Next, we will consider the case where β_1 =0, $\beta_2 >$ 0, for subproblems I(i) and I(ii). Condition (R3) yields

$$\frac{\gamma\beta_2 y^2}{\theta(y)} + \gamma_1(y-1)\left\{(y-1)-[h_1(y)+h_2(y)]\right\} + \gamma_1\alpha\beta_2 M^*(y) > 0$$
$$y^{**} < y < y^* \qquad \text{(R17)}$$

where

$$\theta(y) \triangleq \frac{(1+\mathcal{D}a_2 X^\mu)}{\mathcal{D}a_2 X^\mu} \qquad \text{(R18a)}$$

$$M^*(y) \triangleq (\gamma+\alpha)\beta_2\left(\frac{\mathcal{D}a_2 X^\mu}{1+\mathcal{D}a_2 X^\mu}\right)^2 \qquad \text{(R18b)}$$

$h_1(y)$, $h_2(y)$ are given by (5b) and (5c) respectively.

For (R17) to hold it suffices that

$$\frac{\gamma\beta_2 y^2}{\bar{\theta}} + \gamma_1(y-1)\left\{(y-1)-(\bar{h}_1+\bar{h}_2)\right\} + \gamma_1\alpha\beta_2 \underline{M}^* > 0 \qquad \text{(R19)}$$
$$y^{**} < y < y^*$$

Condition (R19) can be rewritten as

$$y^2(\nu\beta_2+\gamma_1\bar{\theta})-y\gamma_1\bar{\theta}[2+\bar{h}_1+\bar{h}_2]+$$
$$+\gamma_1\bar{\theta}(1+\alpha\beta_2\underline{M}^*+\bar{h}_1+\bar{h}_2)>0,\ y^{**}<y<y^* \qquad \text{(R20)}$$

For (R20) to hold it suffices that

$$\gamma_1\bar{\theta}(2+\bar{h}_1+\bar{h}_2)^2<4(\nu\beta_2+\gamma_1\bar{\theta})*$$
$$*(1+\alpha\beta_2\underline{M}^*+\bar{h}_1+\bar{h}_2) \qquad \text{(R21)}$$

In (21) the following substitutions can be made:

$$\bar{h}_1=2\alpha\beta_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(R22a)}$$

$$\bar{h}_2=\nu\beta_2\left(1+\frac{\mu}{4}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(R22b)}$$

$$\bar{\theta}=\theta(y^{**})<\theta(1)=\frac{(1+\mathcal{D}a_2)}{\mathcal{D}a_2} \qquad \text{(R22c)}$$

because $\theta'(y)<0$.

$$\underline{M}^*=M^*(y^{**})>M^*(1)=(\nu+\alpha)\beta_2\left(\frac{\mathcal{D}a_2}{1+\mathcal{D}a_2}\right)^2 \qquad \text{(R22d)}$$

because $(M^*)'>0$.

Making the above substitutions in (R21) yields

$$\frac{\gamma_1(1+\mathcal{D}a_2)}{\mathcal{D}a_2}\left[2+2\alpha\beta_2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right]^2<$$

$$<4\left[\nu\beta_2+\frac{\gamma_1(1+\mathcal{D}a_2)}{\mathcal{D}a_2}\right]*\left[1+\alpha\beta_2^2(\nu+\alpha)\left(\frac{\mathcal{D}a_2}{1+\mathcal{D}a_2}\right)^2+2\alpha\beta_2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right] \qquad \text{(R23)}$$

For subproblem I(ii) (α =0), (R23) simplifies to

$$\frac{\gamma_1(1+\mathcal{D}a_2)}{\mathcal{D}a_2}\left[2+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right]^2<4\left[\nu\beta_2+\frac{\gamma_1(1+\mathcal{D}a_2)}{\mathcal{D}a_2}\right]*$$

$$*\left[1+\nu\beta_2\left(1+\frac{\mu}{4}\right)\right] \qquad \text{(R24)}$$

REMARK

If we give the parameters the values:

Equation (21)	Equation (33)
$\mu = A$	$\mu = 1/A$
$\gamma_1 = B$	$\gamma_1 = BA$
$\alpha\beta_2 = C$	$\alpha\beta_2 = D$
$\beta_1 = D$	$\beta_1 = C$
$\nu\beta_2 = E$	$\nu\beta_2 = E$

then the figures for (33) will be the same with those of (21) and there is no reason to carry any further calculations.