MULTIPLICITY CRITERIA FOR ISOTHERMAL REACTIONS INVOLVING TWO SPECIES

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In this note, criteria for the existence of multiple steady states in isothermal reactions between two species A and B following a dual site bimolecular Langmuir-Hinshelwood reaction have been studied with reference to a catalytic reactor operated under conditions of complete backmixing. The reaction scheme analysed is

$$A + ZB \longrightarrow \text{products} \tag{i}$$

with the kinetics given by:

$$r = \frac{k_2 AB}{[1 + K_A A + K_B B]^2} \tag{1}$$

The oxidation of CO and hydrogenation of ethylene are examples of reactions following this kinetics. The earlier work in this area has been confined to a situation when the reactant B is in excess and also when $K_B = 0$ [see for example, Matsuura and Kato, 1969, Bukur (1978)]. Thus the kinetics analysed by earlier workers is of the form

$$r = \frac{kA}{[1 + K_A A]^2} \tag{2}$$

In practical situations, the species B may not be in excess and the adsorption equilibrium constant of B may be finite. For example, a typical automobile exhaust stream has a CO percentage of 0.4 to 4.0% and O_2 percentage of 0.13 to 2.1% [see Voltz *et al.*, (1973)]. Hence it is useful to analyse a scheme of the type of Eq. (1) not only because of the generality of the kinetic scheme but also because of its practical implications. The kinetics of the type of Eq. (2) can be reduced as a particular case of Eq. (1) [with $k = k_2 B$ and $K_B = 0$].

We consider here a continuously stirred tank catalytic reactor with a feed rate of F cm^3/sec, having an inlet and exit concentrations of A_0 and A_e for species A, and B_0 and B_e for species B and containing W gms of catalyst. The analysis is restricted to a situation where no external and intraparticle gradients are present.

The governing mass balance equations for the reactant species A and B for this reactor can be written as

$$\frac{F}{W}[A_0 - A_e] = \frac{k_2 A_e B_e}{[1 + K_A A_e + K_B B_e]^2} \tag{3}$$

$$\frac{F}{W}[B_0 - B_e] = \frac{Z k_2 A_e B_e}{[1 + K_A A_e + K_B B_e]^2} \tag{4}$$

The formulation of the problem, as above, is equally valid for a homogeneous reaction in a backmixed reactor with the term W now being replaced by the volume of the reactor. Also it can be noted that the similar equations, with F/W replaced by $3k_g/R\rho_P$ describe the situation for a nonporous catalyst pellet exposed to a bulk gas stream of compositions A_0 and B_0 for the two species respectively. The quantities A_e and B_e for this case would represent the concentration of the respective species at the catalyst surface.

Eliminating B_e in terms of A_e from Eqs. (3) and (4) we have

$$\frac{B_0}{ZA_0} - \left[1 - \frac{A_e}{A_0}\right] = \frac{B_e}{ZA_0} \tag{5}$$

Substituting for B_e from Eq. (5) in Eq. (1) and nondimensionalising it the following equation is obtained:

$$\frac{F}{Wk_2A_0}[1 - a] = \frac{a[q - 1] + a^2}{[1 + K_B^*(q - 1) + a(K_A^* + K_B^*)]^2} \tag{6}$$

Eq. (6) can be arranged as:

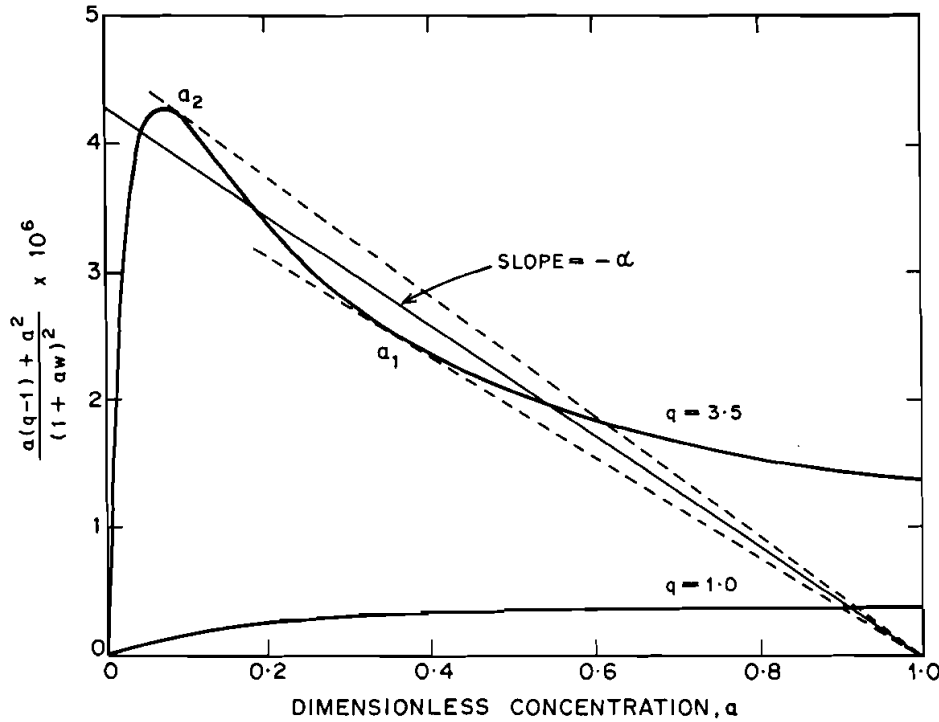$$\alpha[1 - a] = \frac{a[q - 1] + a^2}{[1 + aw]^2} \tag{7}$$

where

$$\alpha = \frac{F[1 + K_B^*(q - 1)]^2}{Wk_2A_0} \tag{8}$$

and

$$w = \frac{K_A^* + K_B^*}{1 + K_B^*[q - 1]} \tag{9}$$

FIGURE 1   Rate *vs* concentration plots for various values of q.

Solution of Eq. (7) gives the concentration of A in the reactor. As the equation is a cubic three real roots are possible for certain cases giving rise to three steady states. Solution of Eq. (7) can be performed graphically. This consists of plotting a graph of $[a(q - 1) + a^2]/[1 + aw]^2$ as a function of a and noting the points of intersection of a straight line passing through $[1, 0]$ and having slope of $[-\alpha]$. Such a plot of $[a(q - 1) + a^2]/[1 + aw]^2$ vs. a is shown in Fig. 1 for two values of the concentration ratio q. It is clearly seen that for $q = 3.5$, three steady states are possible, since the line passing through $[1, 0]$ and having a slope of $[-\alpha]$ cuts the rate curve at three points. It is also seen that for $q = 1$ only one steady state exists. The region of multiplicity for $q = 3.5$ is indicated by the dotted lines which are tangents to the curve from the point $[1, 0]$. Hence multiple steady states can exist if two tangents can be drawn from the point $[1, 0]$ touching the curve in the region $0 < a < 1$. Using this concept a necessary criteria for the existence of multiple steady states can be derived.

The requirement that at the points at which the tangents can be drawn, the slope of the curve $y = [a(q - 1) + a^2]/[1 + wa]^2$ equals the slope of the tangent, leads to an equation

$$a_1^3 + \frac{[2w(q - 1) - 1]}{w} a_1^2 + \frac{[2 - w(q - 1)]}{w} a_1 + \frac{q - 1}{w} = 0 \qquad (10)$$

where a_1 is x-coordinate of one of the points at which the tangent touches the curve.
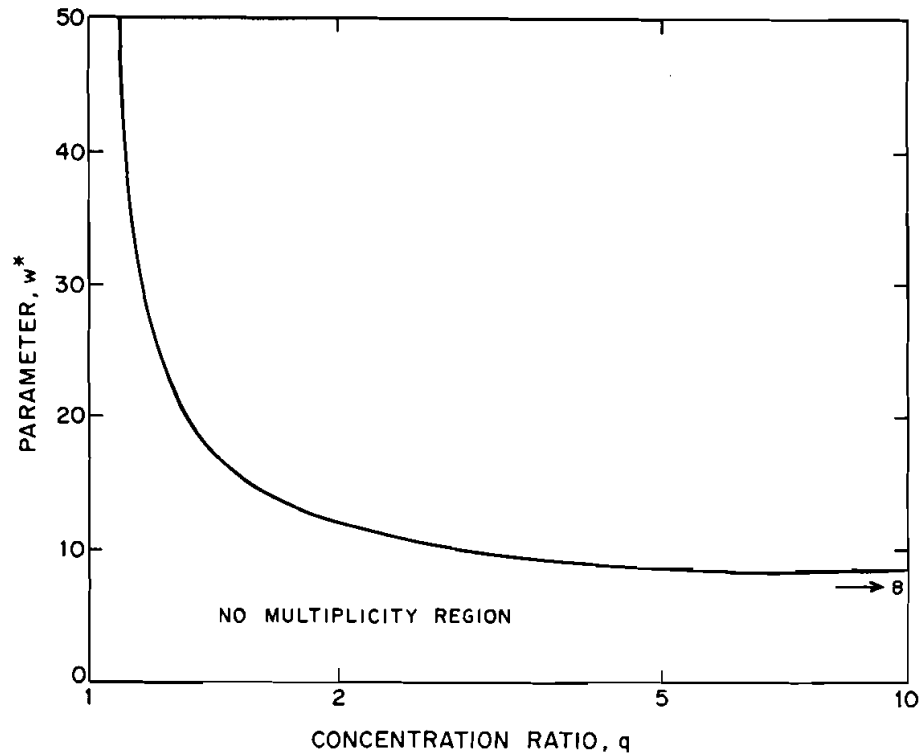
FIGURE 2 Plot of necessary condition for multiplicity.

Eq. (10) is a cubic and the necessary condition for it to have three real roots is:

$$\left[\frac{\beta}{3}\right]^3 + \left[\frac{\gamma}{2}\right]^2 < 0 \tag{11}$$

where

$$\beta = \frac{[2 - w(q - 1)]}{w} - \frac{1}{3}\frac{[2w(q - 1) - 1]^2}{w} \tag{12}$$

$$\gamma = \frac{q - 1}{w} - \frac{1}{3}\left[\frac{2w(q - 1) - 1}{w}\right]\left[\frac{2 - w(q - 1)}{w}\right] + \frac{2}{27}\left[\frac{2w(q - 1) - 1}{w}\right]^3 \tag{13}$$

The criterion (11) is equivalent to saying that for a given q there exists a value of w below which multiple steady states would be absent. This value of w is denoted as w^* and is plotted in Figure 2. For large values of q it is seen that $w^* \rightarrow 8$ which agrees with the result of earlier workers [Luss, (1971)]. Hence the necessary criterion for the existence of multiple steady states is
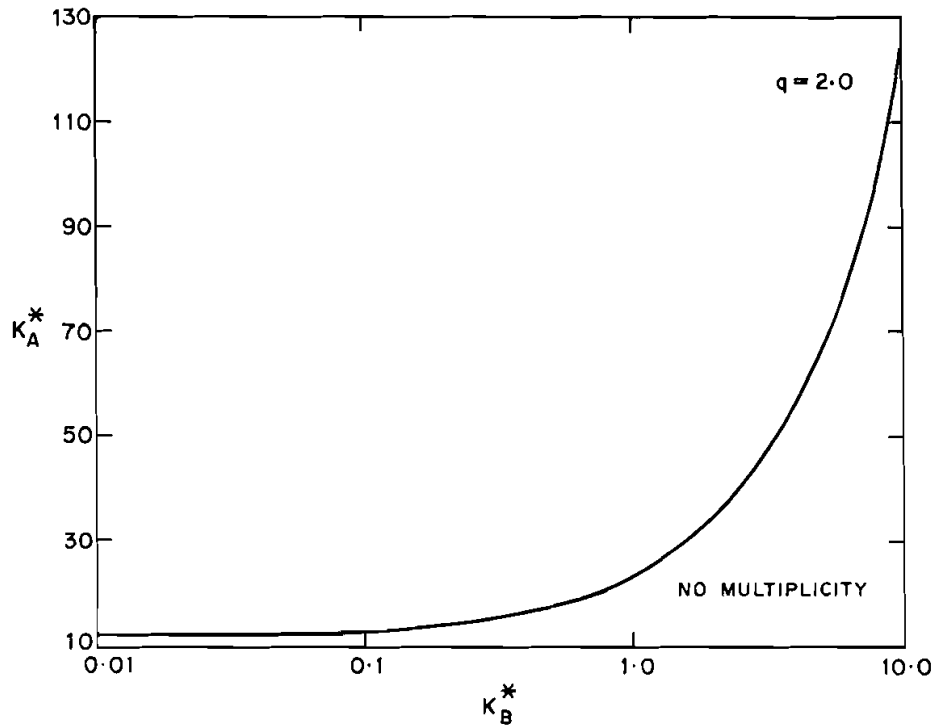
$$w > w^* \tag{14}$$

FIGURE 3   Influence of adsorption of B on the region of multiplicity.

As w is a function of both K_A^* and K_B^* it is interesting to see the influence of adsorption of B on the multiplicity criteria. This is shown in Figure 3 where the minimum value of K_A^* required for multiplicity to exist is shown as function of K_B^* for $q = 2$. As K_B^* increases, a correspondingly larger value of K_A^* is required to obtain multiplicity.

A sufficiency criterion can be obtained by using the same concepts. This can be expressed as

$$G[a_1] < \alpha < G[a_2] \tag{15}$$

where

$$G[a] = \frac{a[q - 1] + a^2}{[1 + aw]^2[1 - a]} \tag{16}$$

and a_1 and a_2 are the points at which the two tangents touch the curve in the region $0 < a < 1$. (See Fig. 1).

A plot of the region of multiplicity is shown in Fig. 4. It is seen that the regions of multiplicity [shown as hatched portion] for $q = 2$ and 10 are markedly different.
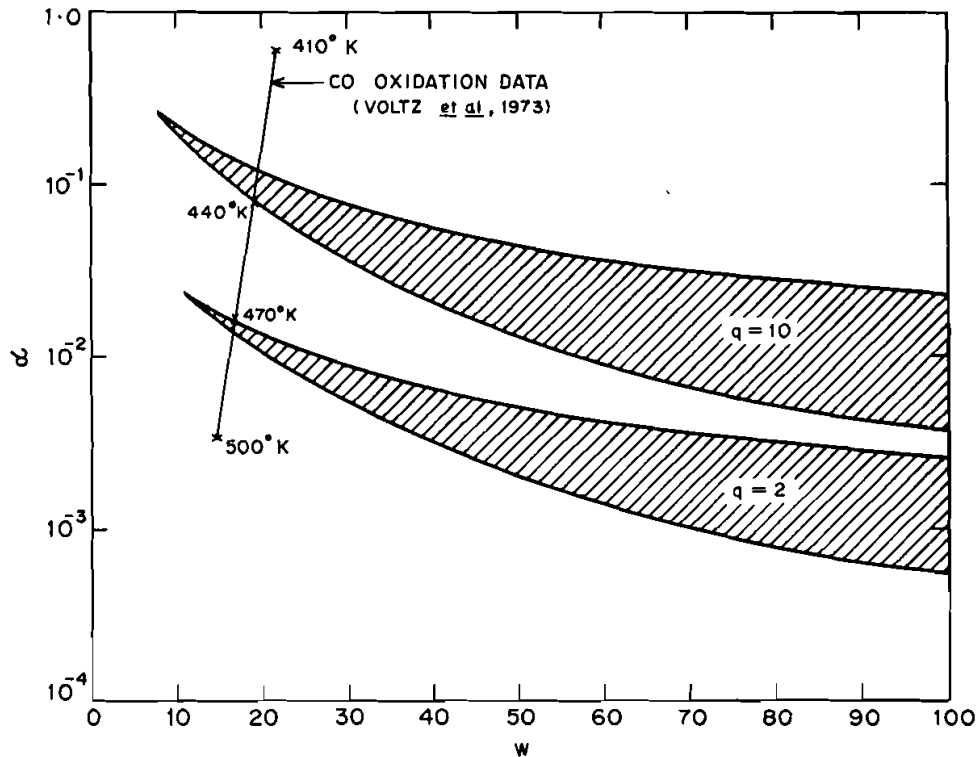
FIGURE 4   Region of multiplicity for various values of q.

Hence it can be concluded that the parameter q strongly influences the region of multiplicity. As an illustration the kinetic data of Voltz et al. (1973) for CO oxidation is used to calculate α and w for various temperatures for $W/F = 0.5$ gm sec/cm^3 and is plotted in Fig. 4. It is seen that for $q = 10$ the multiplicity occurs around a temperature of 440°K while for $q = 2$ the region of multiplicity is much narrower and also occurs at a higher temperature of 470°K.

In conclusion, the effects of the concentration ratio of the reactants and the adsorption equilibrium constants on the region of multiplicity is examined for a Langmuir-Hinshelwood dual site reaction, and it is shown that the criteria for multiplicity is strongly dependent on these two parameters.

NOTATIONS

a	dimensionless concentration of species A, A_e/A_0
A_e	concentration of species A in the exit stream
A_0	concentration of species A in the inlet stream

B_e	concentration of species B in the exit stream
B_0	concentration of species B in the inlet stream
F	feed rate to the reactor
$G[a]$	function defined by Eq. (16)
k, k_2	reaction rate constants
k_g	mass transfer coefficient across the external film
K_A, K_B	adsorption equilibrium constants for species A and B respectively
K_A^*, K_B^*	dimensionless adsorption equilibrium constants defined as $K_A A_0$ and $K_B A_0$ respectively
q	concentration ratio defined as B_0/ZA_0
r	rate of reaction per unit weight of catalyst
R	radius of the catalyst pellet
w	parameter defined by Eq. (9)
w^*	critical value of w for the existence of multiplicity
W	weight of catalyst
Z	Stoichiometric coefficient

Greek Letters

α	parameter defined by Eq. (8)
β	parameter defined by Eq. (12)
γ	parameter defined by Eq. (13)
ρ_p	bulk density of the catalyst

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