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STEADY STATES AND STABILITY ANALYSIS OF A BIMOLECULAR NON-EQUILIBRIUM REACTION SCHEME WITH GENERAL HINSHELWOOD-LANGMUIR SATURATION-INHIBITION LAW

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Résumé. — Nous présentons l'analyse de stabilité d'un schéma réactionnel bimoléculaire à deux variables dans le cas où la loi générale de Hinshelwood-Langmuir d'ordre n , $[X/(1 + qX)^n, n \geq 2]$, est impliquée.

Abstract. — The stability analysis of a simple two-component bimolecular reaction scheme involving a Hinshelwood-Langmuir law of n th-order $[X/(1 + qX)^n, n \geq 2]$, is presented.

Recently [1, 2, 3] the authors have discussed the stability analysis of a simple bimolecular reaction scheme involving a first-order Hinshelwood-Langmuir saturation law. Such a saturation law is of relevance in combustion kinetics [4] and also corresponds to the Michaelis-Menten enzyme kinetics in biochemistry and to the Holling law in Ecology (see Fig. 1). The model reaction scheme is

in which X and Y are variable intermediate reactants, and A and P are products whose concentration is kept constant. All steps in eq. (1) are taken to be irreversible. In eq. (1c) we denote by S/I a saturation/inhibition law of the following type

$$\frac{X}{(1 + qX)^n} \quad (n, \text{ positive integer}) \quad (2)$$

in which n denotes the order of the Hinshelwood-Langmuir law. The general case $n \geq 2$ is of relevance in reactor kinetics [4] (see Fig. 2). In contradistinction to figure 1 the case $n > 1$ in eq. (2) describes a saturation plus inhibitory step in (1). q accounts for the strength of this step.

FIG. 1. — First-order Hinshelwood-Langmuir (Michaelis-Menten-Holling) saturation law.

FIG. 2. — N -th-order Hinshelwood-Langmuir inhibition law ($n \geq 2$). The maximum of the reaction rate is at X_c .

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We associate the following differential equations with the scheme (1), (2) for isothermal processes,

$$\frac{dX}{dt} = XY - \frac{X}{(1 + qX)^n} \quad (3a)$$

$$\frac{dY}{dt} = A - XY \quad (3b)$$

which we take in dimensionless form. The variables X , Y , and A represent dimensionless concentrations.

The stationary solutions of (3) are given by the relations

$$Y_s = A/X_s \quad (4a)$$

$$(1 + qX_s)^n = X_s/A. \quad (4b)$$

There would be as many solutions as there are real and positive roots of the polynomial (4b),

$$\sum_{j=0}^{n-2} \binom{n}{j} X_s^{n-j} q^{n-j} + X_s \left(qn - \frac{1}{A} \right) + 1 = 0. \quad (5)$$

The number of such roots is given by the Harriot-Descartes theorem. We have :

(i) If $Aq > 1/n$, there is no real and positive solution of (6) and so no steady states of (3).

(ii) If $Aq < 1/n$ either we have two steady states or there is none.

In the latter case the alternative is solved by constructing the intersects of $(1 + qX)^n$ with X/A . Therefore two steady solutions of (3) exist if the straight line X/A has a greater slope than the tangent to the curve $(1 + qX)^n$ at the origin. Otherwise there is no steady solution of (3). Thus we have the alternative

a) either

$$Aq > \frac{1}{n \left(\frac{n}{n-1} \right)^{n-1}}; \quad (n \geq 2) \quad (6)$$

and no steady state is available to (3). Rather the concentration grows unbounded : with $Y(t)$ bounded we have $X(t) \rightarrow \infty$ as $t \rightarrow \infty$;

b) or

$$Aq < \frac{1}{n \left(\frac{n}{n-1} \right)^{n-1}}; \quad (n \geq 2) \quad (7)$$

in which case we have two steady states $[X_s^{(1)}, A/X_s^{(1)}]$ and $[X_s^{(2)}, A/X_s^{(2)}]$ such that the following relations hold ($n \geq 2$)

$$X_s^{(1)} < X_0 < X_s^{(2)} \quad (8a)$$

$$X_0 = \frac{1}{q} (n-1)^{-1}. \quad (8b)$$

The (linear) stability of these steady states is given by the eigenvalues of the following matrix

$$\begin{pmatrix} nqA/(1 + qX_s^{(i)}) & X_s^{(i)} \\ -Y_s^{(i)} & -X_s^{(i)} \end{pmatrix}; \quad i = 1, 2 \quad (9)$$

whose characteristic polynomial is

$$\lambda^2 - T\lambda + D = 0 \quad (10a)$$

where

$$T = \frac{nqA}{[1 + qX_s^{(i)}]} - X_s^{(i)}; \quad i = 1, 2 \quad (10b)$$

and

$$D(X_s^{(i)}) = -nqA^2(1 + qX_s^{(i)})^{n-1} + A; \quad i = 1, 2 \quad (10c)$$

From eq. (10c) and the inequality (8a) it follows that

$$D(X_s^{(2)}) < D(X_0) = 0. \quad (11)$$

Thus the $i = 2$ state is a saddle point, and unstable. It has a Poincaré index of (-1) and this precludes the existence of a limit cycle in its neighbourhood. The other steady state ($i = 1$) cannot be a saddle point as $D(X_s^{(1)}) > 0$. It is either (asymptotically) stable or unstable according to the values of T (10b) : $T < 0$ (stable), $T > 0$ (unstable). Besides, it is a focus or a node according to the values of the discriminant $[T^2 - 4D]$: negative (focus), positive (node). Figure 3 gives an illustration of the vector field gene-

FIG. 3. — (a) Qualitative sketch of the vector field defined by eqs. (3), with the separatrices through saddle point « 2 » shown. (b) and (c) Depict the two topologically structurally stable configurations that are possible.

rated by eqs. (3), with the two separatrices shown. The stable separatrix through point « 2 » intersects the X -axis at M , whereas the unstable one moving away from « 2 » goes to infinity as $X(t)$ goes to infinity. To the left of « 2 » the stable separatrix through « 2 » intersects the curves $Y = A/X$, and $Y = 1/(1 + qX)^n$, respectively at N , and P .

Thus we have two topologically structurally stable configurations which are admissible solutions to eqs. (3), as shown respectively in figures 3b and 3c. It is to be noted that the configuration in which the unstable separatrix through « 2 » from its left is also a stable separatrix from the left through « 2 » is structurally unstable, and it has been disregarded here (for details of the stability property used here see the paper by Peixoto [5]).

In the case described in figure 3b application of the Poincaré-Bendixon theorem [6] to the region MNPR ensures the existence of either a limit cycle or an asymptotically stable fixed point in that region. In the case of figure 3c there is either a limit cycle around point « 1 » or if this fixed point is asymptotically stable we have an unstable periodic orbit which is the α -limit of the stable separatrix from above.

In figure 4 we describe the various possible structures that arise. Figure 4a corresponds to the values $\{q = 1, A = 0.2, n = 2\}$ in which case the fixed point « 1 » is asymptotically stable with domain of attraction (stability) restricted to the region MNR. Figure 4b corresponds to $\{q = 2, A = 0.1, n = 2\}$ in which case « 1 » is unstable, and there is bifurcation to a stable limit cycle around « 1 », with domain of attraction the region MNR. Figure 4c corresponds to $\{q = 1, A = 0.1, n = 4\}$: the fixed point « 1 » is unstable and the corresponding configuration to this case is that given in figure 3c. Consequently, for almost all initial conditions the solution of eqs. (3) grows unbounded, as $X(t)$ goes to infinity.

In conclusion, we see that two main differences between the cases $n = 1$ and $n > 1$ are apparent :

- (i) The range of values of A and q for which the solutions to eqs. (3) can be bounded is smaller in the case $n > 1$. In this case it is given by the relation (7) whereas for $n = 1$ it suffices that $Aq < 1$.
- (ii) When $n > 1$, even though the solution of

FIG. 4. — Various possible solutions for the triplet $\{q, A, n\}$: (a) $\{1, 0.2, 2\}$, (b) $\{2, 0.1, 2\}$, (c) $\{1, 0.1, 4\}$.

eqs. (3) may be bounded as time goes to infinity, the steady state and the limit cycle are stable in a finite domain. Thus instability to finite perturbations is expected, which is not the case with $n = 1$.

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