A chemical Lyapunov function

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Consider the reversible dimerization reaction

$$2\,\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{C}.$$

The rate equations are (dispensing with the usual square brackets)

$$\dot{A} = -2k_f A^2 + 2k_r C,$$
$$\dot{C} = k_f A^2 - k_r C.$$

Using either of the rate equations, we find the equilibrium condition

$$\frac{C^*}{(A^*)^2} = \frac{k_f}{k_r}. \tag{1}$$

In order to find the equilibrium point, we have to also use the conservation relation $A+2C = A_0$. It is sufficient for us to know that an equilibrium point exists that satisfies equation (1).

I claim that the following is a Lyapunov function for this system:

$$L(A, C) = A \ln (A/A^*) - A + A^* + C \ln (C/C^*) - C + C^*.$$

We first have to show that it is a positive-definite function for the equilibrium point (A^*, C^*). The first part is easy: By direct substitution, we get $L(A^*, C^*) = 0$. Next, we set out to prove that L reaches a minimum at (A^*, C^*). At a critical point, $\partial L/\partial A = \partial L/\partial C = 0$.

$$\frac{\partial L}{\partial A} = \ln (A/A^*),$$
$$\frac{\partial L}{\partial C} = \ln (C/C^*).$$

The partial derivatives are equal to zero when $A/A^* = C/C^* = 1$, i.e. at the equilibrium point. To prove that we have a minimum, we still need to apply the second derivative test.

$$\begin{aligned}
\frac{\partial^2 L}{\partial A^2} &= \frac{1}{A}, \\
\frac{\partial^2 L}{\partial C^2} &= \frac{1}{C}, \\
\frac{\partial^2 L}{\partial A \partial C} &= 0.
\end{aligned}$$

We have

$$\begin{aligned}
\left.\frac{\partial^2 L}{\partial A^2}\right|_{(A^*,C^*)} &= \frac{1}{A^*} > 0, \\
\left[\frac{\partial^2 L}{\partial A^2}\frac{\partial^2 L}{\partial C^2} - \left(\frac{\partial^2 L}{\partial A \partial C}\right)^2\right]_{(A^*,C^*)} &= \frac{1}{A^* C^*} > 0.
\end{aligned}$$

The second derivative test therefore shows that L has a minimum at (A^*, C^*). This is the only extremum of L, and since $L(A^*, C^*) = 0$, Then $L(A, C) > 0 \in \mathbb{R}_+^2 - (A^*, C^*)$. This completes the proof that L is a positive-definite function for the equilibrium point.

A Lyapunov function is a strictly decreasing function of time (except at the equilibrium point). Thus, consider

$$\begin{aligned}
\dot{L} &= \frac{\partial L}{\partial A}\dot{A} + \frac{\partial L}{\partial C}\dot{C} \\
&= \ln(A/A^*)\left(-2k_f A^2 + 2k_r C\right) + \ln(C/C^*)\left(k_f A^2 - k_r C\right) \\
&= \left(k_f A^2 - k_r C\right)\left[\ln(C/C^*) - 2\ln(A/A^*)\right] \\
&= \left(k_f A^2 - k_r C\right)\ln\left(\frac{C}{A^2}\frac{(A^*)^2}{C^*}\right).
\end{aligned}$$

Now use equation (1):

$$\dot{L} = \left(k_f A^2 - k_r C\right)\ln\left(\frac{k_r C}{k_f A^2}\right).$$

If $k_f A^2 > k_r C$ then the first factor on the right-hand side is positive, but the logarithm is negative, so $\dot{L} < 0$. If, on the other hand, $k_f A^2 < k_r C$, then the first factor is negative and the logarithm is positive, so that $\dot{L}$ is again negative. Therefore $\dot{L} < 0 \in \mathbb{R}^2_+ - (A^*, C^*)$, which makes L a Lyapunov function for the equilibrium point. We can conclude that the equilibrium point is globally stable in $\mathbb{R}^2_+$.