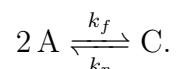


# A chemical Lyapunov function

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Consider the reversible dimerization reaction



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

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

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

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

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,  $\partial L/\partial A = \partial L/\partial C = 0$ .

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

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

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

Now use equation (1):

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

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  $\mathbb{R}_+^2$ .