Electronic Supplementary Information: Entropic analysis of bistability and the General Evolution Criterion

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S1. NON EXACT DIFFERENTIALS

Referring to the rate equations in the main text, we define the three functions

$$F_a(a,x,b) = -k_1 a + k_{-1}x + f([A]_{in} - a), \tag{S1}$$
$$F_x(a,x,b) = k_1 a - k_{-1}x + k_{-2}bx^2 - k_2 x^3, \tag{S2}$$
$$F_b(a,x,b) = k_2 x^3 - k_{-2}bx^2 + f([B]_{in} - b). \tag{S3}$$

Then in order that the differential

$$d\Phi = F_a da + F_x dx + F_b db \tag{S4}$$

be exact, in a simply connected region of composition space, the three functions must satisfy the conditions

$$\left(\frac{\partial F_a}{\partial x}\right) = \left(\frac{\partial F_x}{\partial a}\right), \qquad \left(\frac{\partial F_a}{\partial b}\right) = \left(\frac{\partial F_b}{\partial a}\right), \qquad \left(\frac{\partial F_x}{\partial b}\right) = \left(\frac{\partial F_b}{\partial x}\right). \tag{S5}$$

It is straightforward to check that only the second condition is obeyed, but neither the first nor the last. Hence, there is no kinetic potential Φ.

S2. ALTERNATIVE OPEN-FLOW ARRANGEMENTS

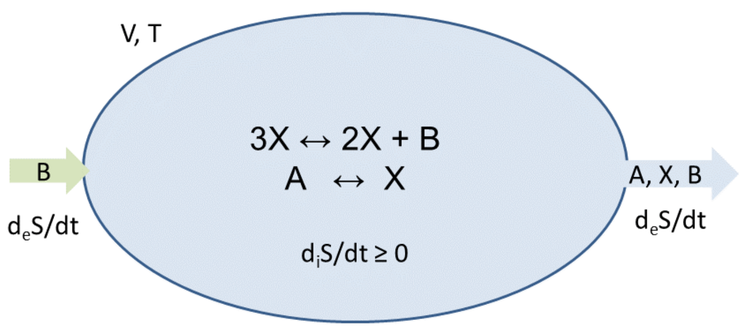

FIG. S1. Alternative open-flow version of the Schlögl model in a well-stirred isothermal reaction tank of volume V. Species B flows in at fixed concentration $[B]_{in}$, and all three species A, X, B flow out with their instantaneous concentrations. The volumetric flow terms give rise to the exchange entropy per unit volume, $\frac{d_e s}{dt}$, which is required for achieving entropy *balance* at any NESS: $\frac{d_i s}{dt} + \frac{d_e s}{dt} = 0$. Compare to Fig. 7 in main text.

The case where only B flows in and all three species A, X, B flow out, as depicted in Fig. S1, gives rise to the following *five* extreme flux modes (EFMs), where each one is made up from a particular subset of one-way reactions and flow terms:

$$\boldsymbol{E}_1 = 3X \to 2X + B,\; B + 2X \to 3X \tag{S6}$$
$$\boldsymbol{E}_2 = A \to X,\; X \to A \tag{S7}$$
$$\boldsymbol{E}_3 = \to B,\; B \to \tag{S8}$$
$$\boldsymbol{E}_4 = \to B,\; B + 2X \to 3X,\; X \to \tag{S9}$$
$$\boldsymbol{E}_5 = \to B,\; B + 2X \to 3X,\; X \to A,\; A \to \tag{S10}$$

$\boldsymbol{E}_1$, and $\boldsymbol{E}_2$ correspond to the two reversible reactions, Eqs. (3,4) in the main text, whereas $\boldsymbol{E}_3$ represents the *unreactive* flow-through of B. The EFM $\boldsymbol{E}_4$ represents the sequence of single reverse reaction driven by the input of B and the output of X. The EFM $\boldsymbol{E}_5$ represents the sequence of the two reverse reactions (see main text) driven by the input of B and the output of A. There is a semi-infinite region of bistability in this particular open flow arrangement. This is easy to see by simply setting $[A]_{in} = 0$ in Eqs. (29-22) (main text). There is then an exact stationary solution in which $[A]^* = [X]^* = 0$ and $[B]^* = [B]_{in}$. This corresponds to the unreactive flow-through of B. This is a thermal equilibrium for each value of $[B]_{in}$, since the entropy production is zero on all these states. The exchange entropy is also zero, hence the balance equation is satisfied trivially on these equilibrium solutions.

This can be contrasted with the case where instead only A flows in and again all three species A, X, B flow out:

$$\boldsymbol{E}_1 = 3X \to 2X + B,\ B + 2X \to 3X \tag{S11}$$

$$\boldsymbol{E}_2 = A \to X,\ X \to A \tag{S12}$$

$$\boldsymbol{E}_3 = \to A,\ A \to \tag{S13}$$

$$\boldsymbol{E}_4 = \to A,\ A \to X,\ X \to \tag{S14}$$

$$\boldsymbol{E}_5 = \to A,\ A \to X,\ 3X \to 2X + B,\ B \to \tag{S15}$$

Here, $\boldsymbol{E}_3$ represents the *unreactive* flow-through of A. The differences in $\boldsymbol{E}_4$ and $\boldsymbol{E}_5$ are clear. There is *no bistability* in this version of open flow.

[1] S. Hoops, S. Sahle, R. Gauges, C. Lee, J. Pahle, N. Simus, M. Singhal, L. Xu, P. Mendes and U. Kummer, COPASI-A COmplex PAthway SImulator. Bioinformatics **22** (2006) 3067-3074.