Oscillating and chaotic entropy production rates (EPR) in chemical systems

Bruce E Hobbs$^{1,2}$ and Alison Ord$^1$

$^1$The University of Western Australia.
$^2$CSIRO.

All chemical systems are thermodynamically nonlinear in that the thermodynamic force (the affinity of the reaction) is not a linear function of the thermodynamic flux (the rate of reaction). Hence only one extremum value of the EPR exists and that is zero at equilibrium. In even the simplest case of a closed, exothermic, chemical system not at equilibrium involving first order kinetics, the EPR fluctuates in time. The only extremal value in EPR for this simple system is the trivial one of zero at equilibrium. If two or more exothermic reactions are coupled or hydrodynamic flows are coupled with the chemical reactions, a range of nonlinear behaviour becomes possible ranging from periodic to chaotic oscillations in EPR. We present some simple examples.