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What is the entropy extremum principle far away from local equilibrium?¹ ELIJAH THIMSEN, Washington University in Saint Louis — Predicting the direction of chemical reactions using thermodynamics requires an entropy extremum principle. Under the governance of local equilibrium, the system evolves towards a stationary equilibrium state, at which entropy attains a constant maximum value. The equilibrium state is constrained by a set of independent state variables, which are often taken to be the temperature, pressure, and relative amounts of different chemical elements. Nonequilibrium systems are classified into two regimes: linear and nonlinear. In the linear regime, it has been argued that the entropy generation rate, which is positive semidefinite according to the 2nd law of thermodynamics, attains a *minimum* value at stationary states. For chemical reactions, a criterion must be fulfilled for operation in the linear regime. The chemical affinity of a reaction must be much smaller than the thermal energy: $A_i/RT_M \ll 1$, where A_i is the chemical affinity, R is the ideal gas constant, and $T_{\rm M}$ is the temperature of the gas. In chemically reactive nonequilibrium plasmas, we have recently demonstrated that stationary states are reached at which $A_i/RT_M >>1$, therefore the system is governed by nonequilibrium, nonlinear thermodynamics. It is currently unknown if an entropy extremum principle governs the nonlinear regime. Discovery of that principle would have immense impact on a broad set of disciplines, for example evolution of life on planet earth. In this presentation, our published experimental data will be used to test a recently proposed hypothesis that systems in the nonlinear regime evolve towards constrained stationary states at which the entropy generation rate is *maximized*.

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