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Epicatalysis: Bending the third principle of catalysis DANIEL SHEEHAN, Department of Physics, University of San Diego — A standard principle of traditional catalysis – that a catalyst cannot alter the final thermodynamic equilibrium of a reaction – can fail in low-pressure, heterogeneous gas-surface reactions [1]. Kinetic theory for this *epicatalysis* is presented, and two well-documented experimental examples are shown: surface ionized plasmas and hydrogen dissociation on refractory metals. This phenomenon should be observable over a wide range of temperatures and pressures, and for a broad spectrum of heterogeneous reactions. By transcending some constraints of equilibrium thermodynamics, epicatalysis might provide new control parameters and synthetic routes for reactions, and enable product streams boosted in thermochemical energy or desirable species. Recent experiments involving hydrogen dissociation on tungsten and rhenium indicate that steady-state nonequilibria can be be maintained between competing epicatalysts within a single blackbody cavity, challenging thermodynamic expectations.

[1] Sheehan, D.P., Phys. Rev. E 88, 032125 (2013).
[2] Sheehan, D.P., D.J. Mallin, J.T. Garamella, and W.F. Sheehan, Found. Phys., in review (2013).

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