281a Structural Constraints on the Microkinetics of Complex Overall Reaction Pathways Comprising Parallel and Sequential Steps

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We have developed a powerful new graph-theoretic approach to determining the reaction route (RR) network architecture as well as kinetics of complex reaction systems. , , A distinct feature of our RR Graphs is that while the branches represent reaction steps comprising the mechanism, the nodes simply represent their interconnectivity, not necessarily individual species, as has been the convention so far, limiting applicability. The nodes are subject to the quasi-steady-state conditions for the intermediates and terminal species. All conceivable pathways with paralle and sequential steps can be traced simply as trails or walks on the RR Graphs. Further, the RR graphs can be directly converted into equivalent electrical circuits, or wiring diagrams, wherein each reaction branch represents an appropriate electrical element, e.g., resistance, reaction rate is akin to branch current, and reaction affinity, or Gibbs free energy change, is like branch voltage, thus allowing well-developed methods of electric circuit theory, including Kirchhoff's voltage and current laws, to be utilized for a rigorous network analysis. The Kirchhoff's laws impose significant structural constraints on the overall reaction kinetics. Thus, once the RR Graph is constructed from a given mechanism, it provides not only the reaction network topology, but can be used to rigorously analyze network kinetics and the dominant pathways and bottleneck steps. We highlight the approach with kinetic analysis of three examples: 1) an enzymatic reaction system, 2) a heterogeneous catalytic process, and 3) an electrochemical example.