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Unusual Quasi-Reversibility (UQR) or Apparent Non-kinetic Hysteresis in Cyclic Voltammetry: An Elaboration upon the Implications of N-shaped Free Energy Relationships as Explanation

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Unusual Quasi-Reversibility (UQR) or Apparent Non-kinetic Hysteresis in Cyclic Voltammetry: An Elaboration upon the Implications of N-shaped Free Energy Relationships as Explanation

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The salient features of unusual quasi-reversibility (UQR) or apparent non-kinetic hysteresis in cyclic voltammetry are 1) Non-identical potentials of the anodic and cathodic peaks which potentials are independent of scan-rate; 2) Peak currents that are proportional to scan-rate (thereby excluding diffusion control as an explanation); 3) Invariance of peak shapes and peak positions with repetitive cycling. The classical "square scheme" combination of heterogeneous and homogeneous kinetics is shown to be an inadequate explanation of UQR. Laviron, and more recently Sadkowski, have invoked the N-shaped free energy curve as the underlying cause of UQR. It is necessary, however, to understand that in the absence of some rate processes that are slow on the time-scale of observation an N-shaped free energy curve will effect reversible (rather than hysteretic) behavior. In the present paper we discuss some general properties of N-shaped free energy curves recapitulating the deduction of their equilibrium (reversible) behavior by application of Gibbs rule of equal areas (or of the Maxwell construction). Arguments are offered why a particular system might exhibit hysteretic (irreversible) behavior. The electrochemical implications of reversible and hysteretic (UQR) behavior are discussed. Several experimental examples of UQR are discussed.

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