

## The Convergence at Equilibrium of Marcus Theory for Electrode Kinetics

Tal M. Nahir<sup>1</sup> and Edmond F. Bowden<sup>2</sup>

<sup>1</sup>Department of Chemistry, California State University, Chico, CA 95929-0210 and <sup>2</sup>Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204

It is often suggested that the interpretation of electron transfer at the electrode-solution interface should be based on a model commonly referred to as Marcus Theory. Approximately a decade ago, through the development and application of alkanethiol-modified gold electrodes, several important experimental contributions appeared to confirm the validity of the Theory as it applies to heterogeneous single electron transfer.<sup>1</sup>

In general, any kinetic model must show a convergence to equilibrium conditions, which may be deduced independently. Therefore, if the mechanism of an electrochemical reaction involves a single step in both forward and backward directions, the rate expressions must result in a convergence to the Nernst equation.<sup>2</sup>

$$\frac{k_{\text{ox}}}{k_{\text{rd}}} = \exp\left(\frac{F\eta}{RT}\right) \quad (1)$$

where  $F$  is the faraday,  $R$  is the universal gas constant,  $T$  is the temperature, and  $\eta$  is the overpotential,

When the distance between the electrode and all redox species is assumed to be identical and constant, and when the electron density in the electrode does not vary with overpotential, the rate constant is an integral:

$$k_{\text{rd}} = A \int_{-\infty}^{\infty} W_{\text{rd}} \frac{1}{1 + \exp\left[\frac{\mp F(\eta' - \eta)}{RT}\right]} d\eta' \quad (2)$$

where  $A$  is a constant, and  $\eta'$  is an integration parameter.  $W$  is the rate constant at  $\eta'$ , and it is also referred to as the density-of-states term.<sup>3</sup> A quadratic relationship between the activation and the reaction free energies yields

$$W_{\text{rd}} = \exp\left[-\frac{(\lambda \pm F\eta')^2}{4\lambda RT}\right] \quad (3)$$

where  $\lambda$  is the reorganization energy (Fig. 1).

The results from the integration of Eq. (2) do show a Nernstian behavior. Interestingly, the smallest rate constants show a larger change with respect to  $\eta$  than what is observed for Butler-Volmer kinetics (Fig. 2). In addition, approximating the Fermi-Dirac distribution with a step function<sup>4</sup> leads to a significant error here (Table 1).

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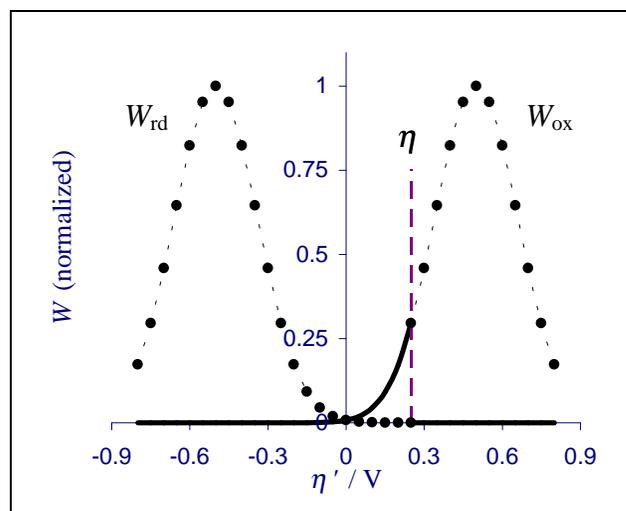


Fig. 1. Dependence of rate constants on  $\eta'$  with  $\lambda=0.5$  eV and  $T=298\text{K}$  (Eq. (3)). Solid lines mark the main regions contributing to the integral in Eq. (2).

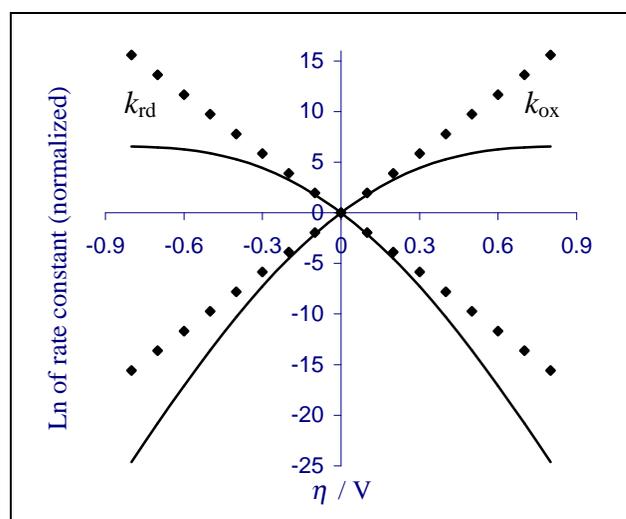


Fig. 2. Dependence of rate constants on overpotential  $\eta$ . Solid lines are calculated from Eq. (2), and squares show results from Butler-Volmer kinetics ( $\alpha=0.5, T=298\text{K}$ ).

$\eta$	From Eq. (2)	Butler-Volmer	Step-function approximation
0	0	0	0
0.1	3.89	3.89	4.24
0.2	7.79	7.79	8.49
0.3	11.68	11.68	12.78
0.4	15.58	15.58	17.12
0.5	19.47	19.47	21.55
0.6	23.36	23.36	26.12
0.7	27.36	27.36	30.87
0.8	31.15	31.15	35.90

Table 1. A comparison among predicted logarithms of the rate-constant ratio  $k_{\text{ox}}/k_{\text{rd}}$  for several overpotentials.