Constrained Variation Calculations of Electron Transfer Transition States Using the Lagrange Method

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This lab has recently made a series theoretical estimates transition states and activation energies (E_a) for elementary charge transfer reactions including, for example, reduction of O_2[1] and oxidation of H_2O[2] bonded to Pt. These properties were determined at various electrode potentials. The model assumption used was that the reaction center is an open system undergoing thermal fluctuations. For an electron to transfer to the reaction center (reduction) or from it (oxidation) when the electrode potential has the value U, the corresponding electron affinity (EA) or ionization potential (IP) of the reaction center will equal $eU + 4.6$ eV, where 4.6 eV connects the standard hydrogen scale (of measurement) to the vacuum scale of (quantum calculations). Since there is an infinite number of structures, $\mathbf{x}_U$, for which the electron transfer condition is satisfied, it is necessary to find the lowest energy one, $\mathbf{x}_U^*$, for this structure is the transition state. Marcus long ago noted this constraint and developed his theory for free energies of activation from it.[3] Once this structure is found, the activation energy, E_a, is then the difference between it's energy, $E(\mathbf{x}_U^*)$ and precursor energy, $E(\mathbf{x}^o)$, where $\mathbf{x}^o$ is the structure of the precursor. In the previous studies the transition states were located by a pattern-search approach to identify the surface of constant EA or IP corresponding to the chosen electrode potential and the lowest energy point on this surface. This is tedious time-consuming procedure which can be improved.

We have developed a new approach to the problem of finding electron transfer transition states using the Lagrange method of undetermined multipliers.[4] We find a stationary point $\mathbf{x}^*$, in the Lagrangian function

$$\Lambda(\mathbf{x}, \lambda) = \varphi(\mathbf{x}) - \lambda[\psi(\mathbf{x}) - E_e(U)] \tag{1}$$

where $E_e(U)$ is the electron energy and

$$\varphi(\mathbf{x}) = E_O(\mathbf{x}) - E_O(\mathbf{x}^o) \tag{2}$$

and, for a reduction reaction,

$$\psi(\mathbf{x}) = E_R(\mathbf{x}) - E_O(\mathbf{x}) \tag{3}$$

where $E_R(\mathbf{x})$ is the energy of the reduced system and $E_O(\mathbf{x})$ is the energy of the oxidized system; for an oxidation reaction, interchange R and O. The conditions for stationary points are

$$\partial\Lambda(\mathbf{x}^*)/\partial\lambda = 0 \tag{4}$$

and

$$\nabla \Lambda = 0 \tag{5}$$

Gradients used in Eq. 5 are calculated by finite differences.

Directions are chosen so that once an initial structure is found, the precursor structure being a convenient one since it is easily calculated and has zero activation energy at a well-defined potential, transition states at new potentials are found rapidly by the steepest decent method. Several iterations are needed, as shown if Fig. 1 for oxidation of H_2O bonded to Pt, with five internuclear distances varied. The starting point is at the far right at zero energy; it is the oxidation precursor.

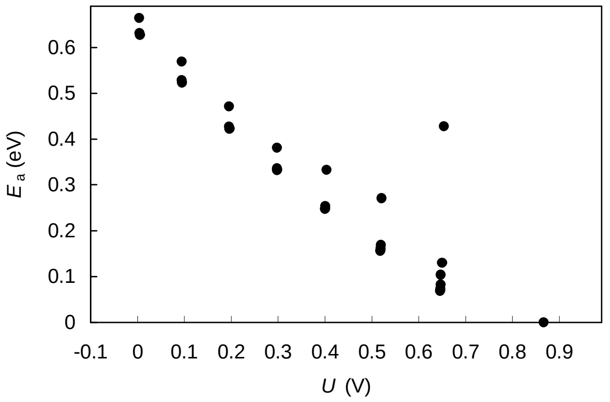

Figure 1. Convergence to $E_a(U)$ by successive iterations.

The lowest energy points in Fig. 1 are the final results of a series of iterations at each chosen potential. They are the predicted activation energies for these potentials. They and additional results are graphed in Fig. 2 along with results obtained using the pattern-search approach from Ref. 2. The new application based on the Lagrange method produces more accurate and uniform results with relatively little computational effort.

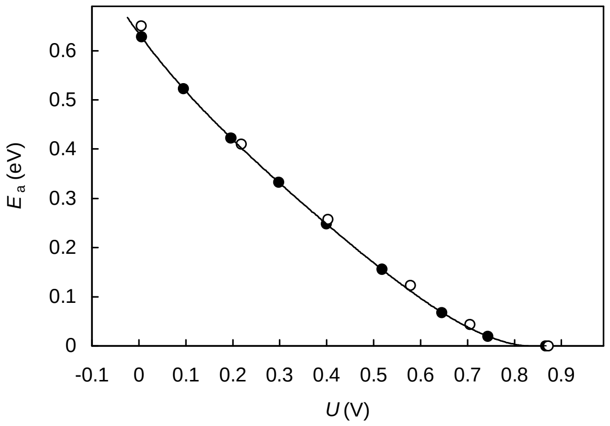

Figure 2. Comparison of pattern-search (open circles) and current constrained variation results (closed circles).

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References

1. R. A. Sidik, A. B. Anderson, *J. Electroanal. Chem.*, **528**, 69 (2002).
2. A. B. Anderson, N. M. Neshev, R. A. Sidik, P. Shiller, *Electrochim. Acta*, **47**, 2999 (2002).
3. R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).
4. R. Fletcher, *Practical Methods of Optimization*, John Wiley & Sons Ltd., Chichester (1987).