ADDITIONS AND CORRECTIONS

1990, Volume 94

R. A. Marcus: Theory of Electron Transfer Rates across Liquid−Liquid Interfaces

There are several typos in some intermediate equations in this article, as follows. (The initial eqs 2.2 and 2.3 and the final eqs 3.6−3.8 of the derivation are unaffected.)

Page 4154. A minus sign should precede the first term of the exponent, $(E - E^\circ)ne/2k_BT$, in eq 3.2 and the exponent $\alpha xne/k_BT$ in eq 3.4. The $c_{r,2}$ and $c_{0,2}$ should be deleted from eq 3.5. A correction to eq 2.11 was mentioned earlier.[1]

Perhaps it should be stressed that the key equations are eqs 2.2 and 2.3, which, when specialized to the cyclic voltammetry liquid−liquid interface experiments of Schiffrin and co-workers,[2] yield eqs 3.6−3.8. For other types of experiments eqs 2.2 and 2.3 would be used, or, if eq 2.10 is introduced, eq 2.12:

$$k_0 = [2\pi(a_1 + a_2)\Delta R/\kappa\nu]k_1^{el}k_2^{el} \exp\left[\frac{-\Delta G^\circ}{2k_BT} + \frac{\Delta G^{\circ 2}}{4\lambda k_BT}\right] \quad (2.12)$$

where the various symbols are defined in the article. The typical units of k_0 are cm^4 $molecule^{-1}$ s^{-1} or, using the standard conversion factor of 6.02×10^{20}, M^{-1} cm s^{-1}. The latter units appear in the article. (The analogous units for the bimolecular collision frequency in the literature, $(8\pi k_BT/\mu)^{1/2}\sigma^2$, have typically been cm^3 $molecule^{-1}$ s^{-1} or, with the similar conversion, M^{-1} s^{-1}.[3]) Equation 2.12 for the case of $\Delta G^\circ = 0$ is given earlier in ref 1 and in eq 9 of ref 4.

(1) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 7242.

(2) E.g.: Geblewicz, G.; Schiffrin, D. J. *Electronal. Chem.* **1988**, *244*, 27.(3) E.g.: Steinfeld, J. I.; Francisco, J. S.; Hase, J. W. *Chemical Kinetics and Dynamics* Prentice-Hall: Engelwood Cliffs, 1989; p 247.

(4) Marcus, R. A. *J. Phys. Chem.* **1991**, *95*, 2010.

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Page 2012. In eqs 17 and 18 the right-hand sides should be multiplied by 10^{-3}, which makes the thick layer model closer to the available experimental result. However, as stressed in the article the current uncertainties in the electrochemical rate constants k_1^{el} and k_2^{el} used in the calculation make the comparison uncertain at this time, and more experimental data are needed. I believe the factor of 10^{-3} was first called to my attention by Professor David Schiffrin.

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