

The Function Describing the Peak Potential Separation During Cyclic Voltammetry of Fast Heterogeneous Charge Transfer Reactions

ELISABET AHLBERG and
VERNON D. PARKER*

Laboratory for Organic Chemistry, Norwegian
Institute of Technology, University of Trondheim,
N-7034 Trondheim-NTH, Norway

During the past fifteen years since Nicholson¹ presented his calculations on the peak potential separations during cyclic voltammetry of quasi-reversible one electrode processes, eqn. (1) and the theoretical data have been applied in determining the heterogeneous charge transfer rate constants of numerous redox systems.²⁻⁶ In the expression, $\gamma = (D_o/D_r)^{1/2}$ where D_o and D_r are the diffusion coefficients of the oxidized and reduced species, α is the transfer coefficient, v is the voltage sweep rate and the other symbols have their usual significance. The manner in which the theoretical

$$\psi = \gamma^\alpha k_s / (\pi D_o F v / RT)^{1/2} \quad (1)$$

data are normally used is to construct a working curve where ψ is plotted as a function of the peak separation (ΔE^p) and experimental values of ΔE^p can then be used to determine ψ and hence, k_s .

Such an analysis procedure is not directly applicable to systems for which ψ is greater than 7 since this is the limit stated by Nicholson¹ where the response becomes identical to that for a Nernstian process. Great improvements in instrument design and capability have been made since 1965 and thus this limitation no longer holds. We have recently reported cyclic voltammetric peak potential data with a precision of the order of 0.2 mV⁷ and thus a wide unexplored potential region, ΔE^p between 63 and 59 mV, exists where measurements could provide rate constants for very rapid heterogeneous charge transfer. Another problem is the precision in the theoretical data which was only reported to 1 mV, presumably because this was higher than the experimental precision at that time.¹ For this reason, we have reexamined the relationship between ψ and ΔE^p in order to extend the use of eqn. (1) to higher values of ψ .

We have found that eqn. (2) precisely gives the values of ΔE^p from the values of ψ previously reported.¹ The comparison of ΔE^p values calculated

Table 1. Comparison of peak potential separations calculated by numerical methods and by series expansion.

ψ	ΔE^p /mV		
	Series ^a	Series ^b	Nicholson ^c
20	60.30(0.70) ^d	61.01(0.01) ^d	61
7	62.53(0.47)	63.27(0.27)	63
6	63.10(0.90)	63.85(0.15)	64
5	63.90(1.10)	64.66(0.34)	65
4	65.10(0.90)	65.87(0.13)	66
3	67.10(0.90)	67.90(0.10)	68
2	71.10(0.90)	71.95(0.05)	72
1	83.10(0.90)	84.09(0.09)	84
0.75	91.11(0.89)	92.19(0.19)	92

^a ΔE_{rev}^p equal to 59.2 mV. ^b 59.8 mV substituted for ΔE_{rev}^p . ^c From Ref. 1. ^d Values in parentheses are the differences between the values calculated and those given in Ref. 1.

Table 2. Comparison of peak potential separations calculated by digital simulation and by series expansion.

ψ	$\Delta \Delta E^p$	
	Series ^a	Simulation
1556	0.02 (0.02) ^b	0
1000	0.02 (0.02)	0
100	0.24 (0.04)	0.2
50	0.47 (0.07)	0.4
20	1.18 (0.18)	1.0
7	3.38 (0.22)	3.6
6	3.94 (0.46)	4.4
5	4.73 (0.27)	5.0
4	5.91 (0.29)	6.2

^a From eqn. (2). ^b Values in parentheses are the differences in the values calculated by the two methods.

$$\Delta \Delta E^p = \Delta E^p - \Delta E_{rev}^p = (\ln 10)RT/F(2^{-1} - 2^{-3} + 2^{-5})\psi^{-1} \quad (2)$$

using (2) with the theoretical values is shown in Table 1. The correct value of ΔE_{rev}^p (59.2 mV), that for a Nernstian charge transfer under the conditions of the calculations,* led to ΔE^p values which were consistently about 0.8 mV less than those reported by Nicholson. The best agreement was found when

* ΔE^p is dependent upon the switching potential and corresponds to 59.2 mV for ΔE_{rev}^p , under the conditions of the calculations.

* Author to whom correspondence should be addressed.

ΔE_{rev}^p was replaced by 59.8 mV, in which case the average deviation was a mere 0.15 mV. It should be pointed out that the agreement deteriorates for ψ values lower than 0.75.

In order to be sure that ψ is a continuous function up to values corresponding to the diffusion controlled limit, ΔE^p values for large k_s were obtained by digital simulation.⁸ The data from the simulations as well as that calculated using eqn. (2) are summarized in Table 2. The simulation assumed α equal to 0.5 and the frequency of the time steps was such that the potentials are accurate to ± 0.2 mV. Once again, the data obtained by simulation and by the series expansion (2) were identical within the limits of the error of the simulation. The average deviation was equal to 0.13 mV.

From the comparisons shown in Tables 1 and 2, we conclude that eqn. (2) gives as precise values of ΔE^p from a given ψ value as either the numerical method of Nicholson¹ or digital simulation. Since the equations describing the kinetic-diffusion problem cannot be solved analytically,¹ we see no way at this time of relating eqn. (2) to an analytical solution.

From a practical point of view, this work has opened up the ΔE^p region from 63 to 59 mV for heterogeneous charge transfer rate studies. With a precision of about 0.2 mV, it should be possible to estimate ψ values up to about 100. At 1 kV s⁻¹ sweep rate, this corresponds to a heterogeneous rate constant of about 110 cm s⁻¹ assuming a D value of 10⁻⁵ cm² s⁻¹. We are actively investigating the kinetics of rapid charge transfer by this method.

Acknowledgement. We thank the Norwegian Research Council for Science and the Humanities for support for E. A.

1. Nicholson, R. S. *Anal. Chem.* 37 (1965) 1351.
2. Perone, S. P. *Anal. Chem.* 38 (1966) 1158.
3. Capon, S. P. and Parsons, R. *J. Electroanal. Chem.* 46 (1973) 215.
4. Rosanske, T. W. and Evans, D. H. *J. Electroanal. Chem.* 72 (1976) 277.
5. Sharp, M. J. *Electroanal. Chem.* 88 (1978) 193.
6. DePalma, R. A. and Perone, S. P. *Anal. Chem.* 51 (1979) 829.
7. Ahlberg, E., Svensmark, B. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 47.
8. Feldberg, S. *Electroanal. Chem.* 3 (1969) 199.

Received October 18, 1979.