

# Simulation Protocol of Simple Diffusional Electrode Mechanism in Square-Wave Voltammetry

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## Abstract

A working protocol for calculation of square-wave voltammograms of a simple diffusional electrode transformation of water soluble redox couple is presented in the simulation package MATHCAD. We give the readers all parameters and the recursive formula needed to calculate the voltammograms of this electrode mechanism relevant to describe the voltammetric behavior of many water-soluble proteins and enzymes.

The screenshot shows the MathCAD software interface with the following content:

**Parameters:**  $dE := 0.008$ ,  $E_{sw} := 0.05$ ,  $\Delta E := 0.6$ ,  $k := 1 \cdot \frac{\Delta E}{dE} \cdot 50$ ,  $E_s := 0.25$ ,  $f := 50$ ,  $d := \frac{1}{(50 \cdot f)}$ ,  $F_{\infty} := 96500$ ,  $n := 1$ ,  $k_s := .025$ ,  $D := 4 \cdot 10^{-6}$ ,  $\alpha := 0.5$ ,  $R_{\infty} := 8.314$ ,  $T_{\infty} := 298.15$

**Equation (I):** 
$$\text{potential}_k := \left( \text{ceil} \left( \frac{k}{25} \cdot \frac{1}{2} \right) \cdot dE + \text{if} \left( \frac{\text{ceil} \left( \frac{k}{25} \right)}{2} = \text{ceil} \left( \frac{k}{25} \cdot \frac{1}{2} \right), 1, -1 \right) \cdot E_{sw} + E_{sw} \right) - dE$$

**Equation (II):** 
$$P_k := E_s + E_{sw} - \text{potential}_k$$

**Equation (III):** 
$$\phi_{\infty k} := n \frac{F}{R \cdot T} \cdot P_k$$

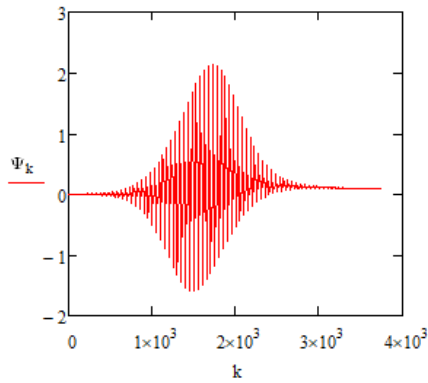
**Equation (IV):** 
$$S_{\infty k} := \sqrt{k} - \sqrt{k-1}$$

**Equation (V):** 
$$K_{\infty k} := \frac{k_s}{\sqrt{D \cdot f}}$$
 (K is dimensionless rate parameter related to electron transfer step)

**Graph (graph1):** A plot of  $P_k$  versus  $k$ . The x-axis ranges from 0 to  $4 \times 10^3$  with major ticks at  $1 \times 10^3$ ,  $2 \times 10^3$ , and  $3 \times 10^3$ . The y-axis ranges from -0.4 to 0.4 with major ticks at -0.4, -0.2, 0, 0.2, and 0.4. The data is represented by a series of red vertical bars that form a downward-sloping staircase pattern, starting at  $P_k \approx 0.3$  for  $k=0$  and ending at  $P_k \approx -0.35$  for  $k=4000$ .

$$\Psi_1 := \frac{K \cdot e^{-\alpha \cdot \Phi_1}}{1 + 2 \cdot K \cdot \left[ \frac{1}{(50 \cdot \pi)} \cdot \frac{1}{2} \cdot (1 + e^{\Phi_1}) \right] \cdot e^{-\alpha \cdot \Phi_1}} \quad (\text{V})$$

$$\Psi_k := \frac{K \cdot e^{-\alpha \cdot \Phi_k} \left[ 1 - 2 \cdot (50 \cdot \pi) \cdot \frac{1}{2} \cdot (1 + e^{\Phi_k}) \cdot \sum_{j=1}^{k-1} (\Psi_j \cdot S_{k-j+1}) \right]}{1 + 2 \cdot K \cdot \left[ \frac{1}{(50 \cdot \pi)} \cdot \frac{1}{2} \cdot (1 + e^{\Phi_k}) \right] \cdot e^{-\alpha \cdot \Phi_k}}$$



(graph2)

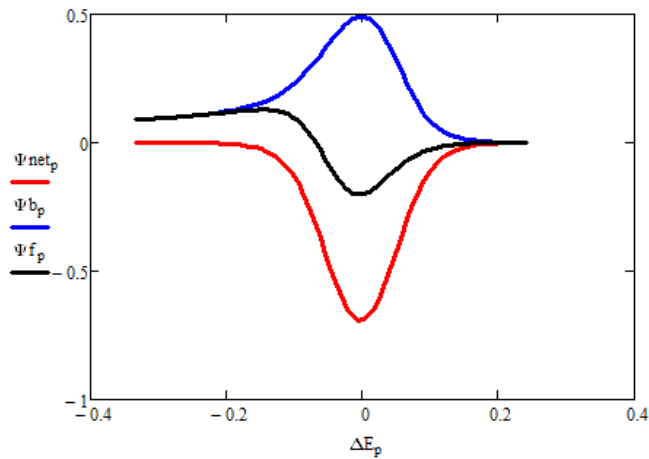
$$p := 1 \cdot \frac{\Delta E}{dE} - 2$$

$$\Psi_{b_p} := \Psi_{(p+1) \cdot 50} \quad (\text{VII})$$

$$\Psi_{f_p} := \Psi_{50 \cdot p + 25} \quad (\text{VIII})$$

$$\Psi_{net_p} := \Psi_{f_p} - \Psi_{b_p} \quad (\text{IX})$$

$$\frac{\Delta E}{\Delta \Phi} := E_s - (p) \cdot dE \quad (\text{X})$$



(graph3)

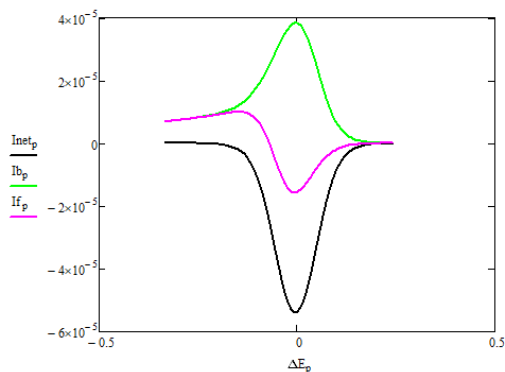
$$A_{ox} = 0.0314 \quad c_{Ox} = 1 \cdot 10^{-6}$$

$$(XI) \quad (XII)$$

$$I_{f_p} = \frac{(\Psi_f)_p}{0.55} F A \sqrt{D} \bar{f} c_{Ox} \quad (XIII)$$

$$I_{b_p} = \frac{(\Psi_b)_p}{0.55} F A \sqrt{D} \bar{f} c_{Ox} \quad (XIV)$$

$$I_{net_p} = I_{f_p} - I_{b_p} \quad (XV)$$



(graph4)

$\Psi_{net_p} =$	$\Psi_f_p =$	$\Psi_b_p =$	$\Delta E_p =$
-5.065·10 <sup>-4</sup>	-9.165·10 <sup>-5</sup>	4.148·10 <sup>-4</sup>	0.242
-6.997·10 <sup>-4</sup>	-1.511·10 <sup>-4</sup>	5.487·10 <sup>-4</sup>	0.234
-9.579·10 <sup>-4</sup>	-2.189·10 <sup>-4</sup>	7.39·10 <sup>-4</sup>	0.226
-1.309·10 <sup>-3</sup>	-3.063·10 <sup>-4</sup>	1.002·10 <sup>-3</sup>	0.218
-1.786·10 <sup>-3</sup>	-4.225·10 <sup>-4</sup>	1.363·10 <sup>-3</sup>	0.21
-2.436·10 <sup>-3</sup>	-5.788·10 <sup>-4</sup>	1.857·10 <sup>-3</sup>	0.202
-3.321·10 <sup>-3</sup>	-7.899·10 <sup>-4</sup>	2.531·10 <sup>-3</sup>	0.194
-4.526·10 <sup>-3</sup>	-1.075·10 <sup>-3</sup>	3.451·10 <sup>-3</sup>	0.186
-6.162·10 <sup>-3</sup>	-1.46·10 <sup>-3</sup>	4.702·10 <sup>-3</sup>	0.178
-8.383·10 <sup>-3</sup>	-1.979·10 <sup>-3</sup>	6.405·10 <sup>-3</sup>	0.17
-0.011	-2.677·10 <sup>-3</sup>	8.714·10 <sup>-3</sup>	0.162
-0.015	-3.613·10 <sup>-3</sup>	0.012	0.154
-0.021	-4.864·10 <sup>-3</sup>	0.016	0.146
-0.028	-6.529·10 <sup>-3</sup>	0.022	0.138
-0.038	-8.731·10 <sup>-3</sup>	0.029	0.13
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