# Two Regenerative Chemical Reactions Associated to the two Electron Transfer Steps of a Diffusional EE Mechanism-Theory of EC’EC’ Mechanism in Square-Wave Voltammetry

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## Abstract

While many water-soluble redox enzymes often undergo an electrochemical redox transformation in two consecutive electron transfer steps, it is very common situation under physiological conditions to have two different regenerative steps associated to both electron transfer steps of the so-called diffusional EE Mechanism. In this work, for the first time the theory of an EC’EC’ mechanism is presented, while model is solved under conditions of square-wave voltammetry. By simulating this important electrochemical mechanism, one can get relevant set of data about kinetics and mechanism of interactions between important redox enzymes and various substrates.

**TWO STEP DIFFUSIONAL EC'EC'cat Mechanism in SWV---new version**

$EsI := 0.35$ $\quad \Delta E := 1$ $\quad dE := 0.01$ $\quad Esw := 0.05$ $\quad EsII := 0.65$ $\quad r := 1..1$

$n := 1$ $\quad F := 96500$ $\quad R := 8.314$ $\quad T := 298.15$

$KI_r := 10^{.75 \cdot r}$

$KII := 10^{.75}$

$j := 1..\frac{\Delta E}{dE} \cdot 50$

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$ $\quad \log(KI_r) =$

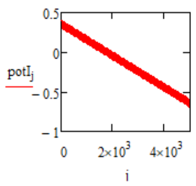
$\lambda := 1.0612400001$

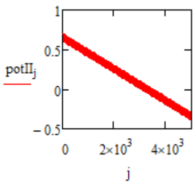
$KI_1 = 5.623$

λ e kineticki parametar na ireverzibilna hemiska reakcija
povrzana so prv elektroden cekor

$$potI_j := EsI + Esw - \left[ \left( ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left( \frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1 \right) \cdot Esw + Esw \right) - dE \right]$$

$$potII_j := EsII + Esw - \left[ \left( ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left( \frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1 \right) \cdot Esw + Esw \right) - dE \right]$$





$$M1_j := \sqrt{\frac{j}{1}} - \sqrt{\frac{j-1}{1}}$$

$$A_j := \left(1 - erfc\left(\sqrt{\frac{\lambda}{50 \times 1} \cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{\lambda}{50 \times 1} \cdot (j-1)}\right]\right]$$

$$B_j := \left(1 - erfc\left(\sqrt{\frac{z}{50 \times 1} \cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{z}{50 \times 1} \cdot (j-1)}\right]\right]$$

$$\Phi I_j := n \cdot \frac{F}{R \cdot T} \cdot potI_j \quad \Phi II_j := n \cdot \frac{F}{R \cdot T} \cdot potII_j$$

$z := .001$

z e kataliticki parametar vo ovoj
model povrzan so vtor cekor

$x := 0.001$

$$\Psi I_{1,r} := \frac{\frac{KI_r}{1} \cdot e^{-\alpha 1 \cdot \Phi I_1} - 0}{1 + KI_r \cdot \lambda^{-.5} \cdot A_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + 1 \lambda^{-.5} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot A_1}$$

$$\Psi II_{1,r} := \frac{\lambda^{-.5} KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{1 + \frac{KII \cdot M1_1 \cdot 2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right)} \cdot \Psi I_{1,r} \cdot A_1$$

$\Psi I_{1,1} = 6.112 \times 10^{-6}$

$\Psi II_{1,1} = 0$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{1}{\sqrt{\lambda}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - KI_r \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\lambda}} \cdot A_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot A_1 \cdot KI_r}$$

$$\Psi II_{j,r} := \frac{KII \frac{1}{\sqrt{\lambda}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - KII \frac{0}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - \frac{0}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M1_{j-i+1}\right) - \frac{1}{\left(\sqrt{z}\right) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{\left(\sqrt{z}\right) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + KII \frac{A_1 \cdot 0}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} + \frac{0 M1_1}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{\left(\sqrt{z}\right) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{\left(\sqrt{z}\right) \cdot (1+0)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$

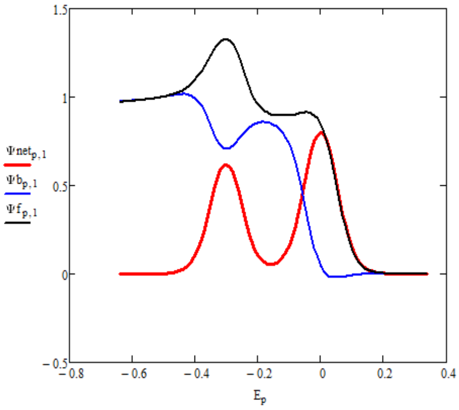
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

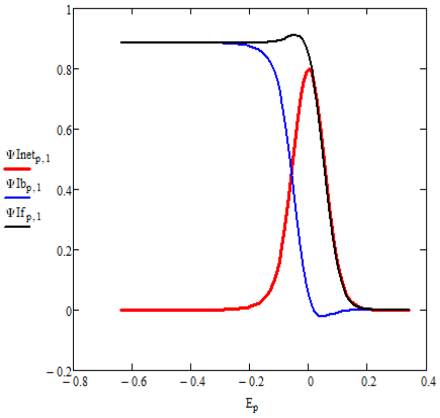
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

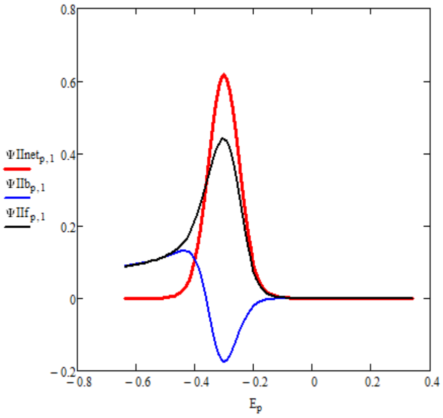
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

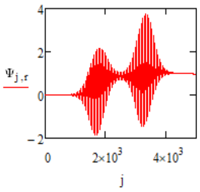
$E_p := EsI - p \cdot dE$

$\Psi b_{p,r} := \Psi_{50 \cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1) \cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$







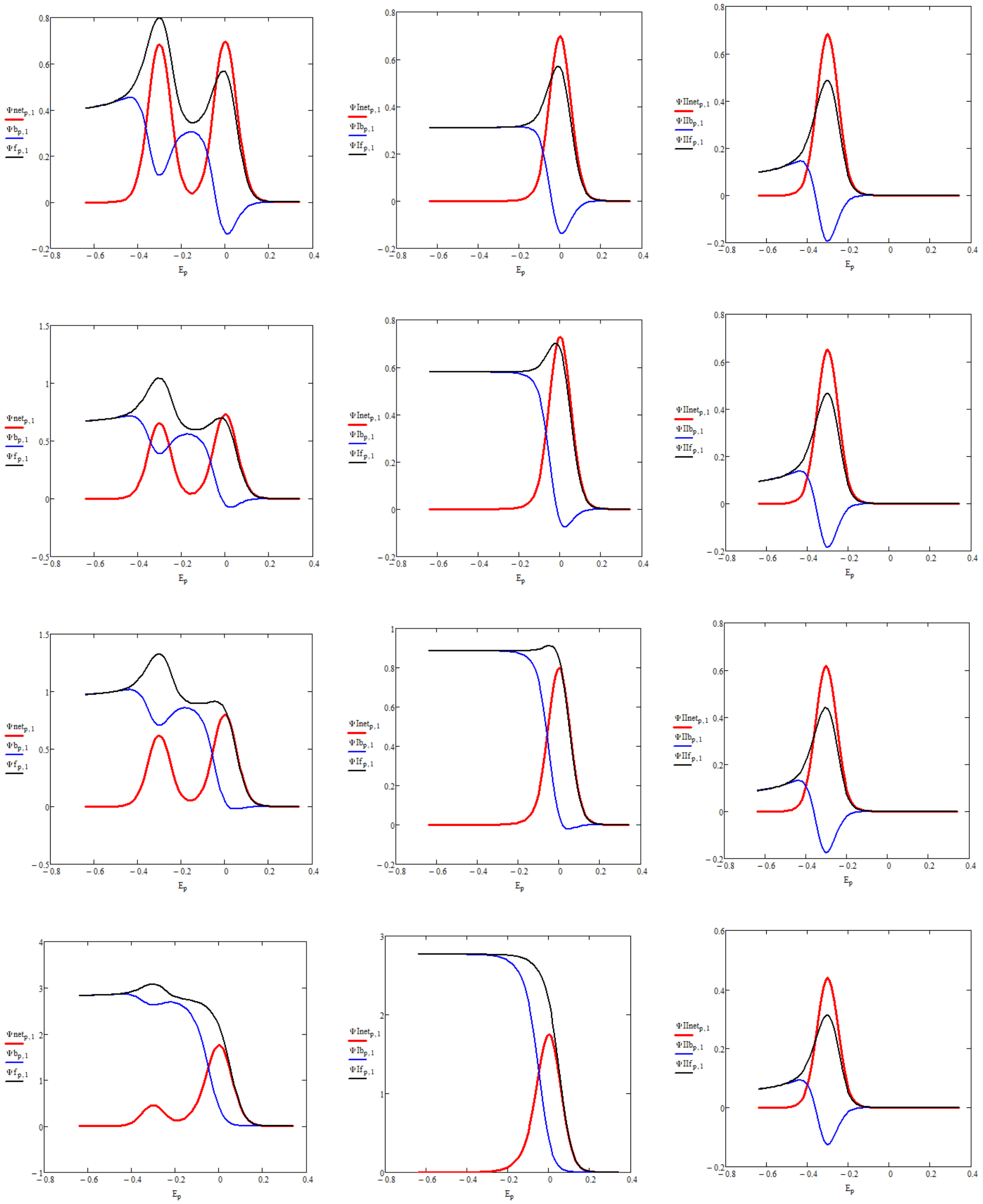


$\Psi f_{p,1} =$

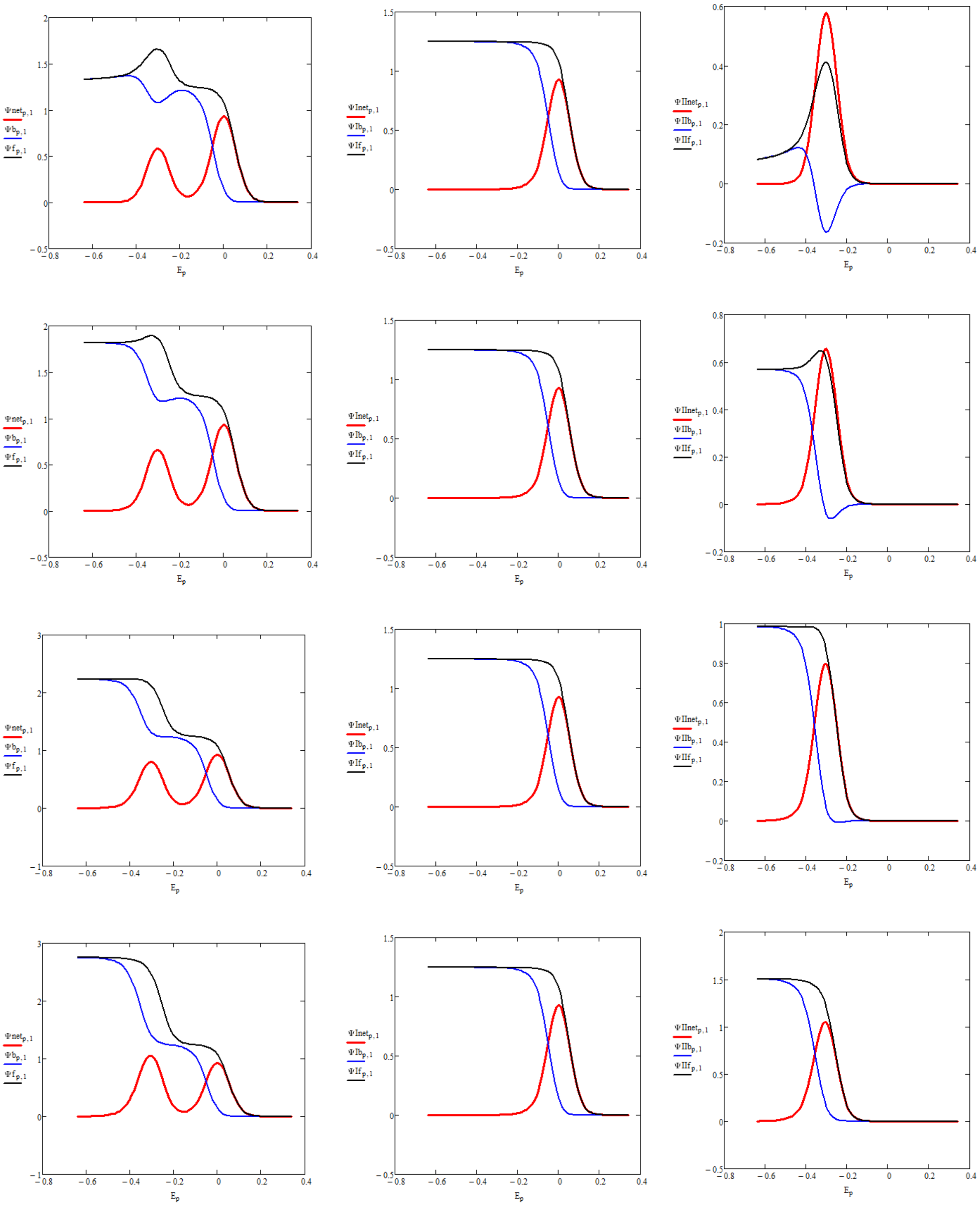
$\Psi b_{p,1} =$

$\Psi net_{p,1} =$

$E_p =$



**Effect of the rate of the regenerative chemical step coupled to first electron transfer, in conditions of no regenerative reaction associated to the second electrochemical step.**



Effect of the rate of the regenerative chemical reaction associated to the second electron transfer step, in conditions of moderate catalysis to the first electrochemical step.

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