ALL-in-ONE VOLTAMMETRY: Theoretical simulation of the ECrevEC' mechanism allows studying of all common mechanisms from a single theoretical model

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Abstract

The ECrevEC′ regenerative two-step electrode mechanism represents a comprehensive and unifying kinetic framework that covers a wide range of classical electrochemical mechanisms as limiting cases. This mechanism consists of two consecutive electron-transfer steps separated by a reversible homogeneous chemical reaction, followed by a regenerative chemical reaction that couples the product of the second electron transfer back to the electroactive species. Depending on the magnitude of the equilibrium constant of the interim chemical step (Keq), the chemical rate parameter governing this equilibrium (Kchem), and the kinetic rate constant of the regenerative reaction (kc), the ECrevEC′ mechanism can smoothly reproduce the characteristic behavior of the simple "E mechanism", the ECrev, CErev, EC′ (regenerative), the ECE, the EEC' and EE mechanisms, as well.

Theoretical modeling of this complex reaction scheme is of central importance, as it enables a systematic exploration of the full mechanistic space within a single mathematical formalism. By adjusting dimensionless kinetic and thermodynamic parameters, transitions between different limiting cases can be quantitatively described without altering the underlying reaction scheme. Such modeling provides deep insight into the interplay between electron-transfer kinetics, chemical equilibria, and homogeneous regeneration processes.

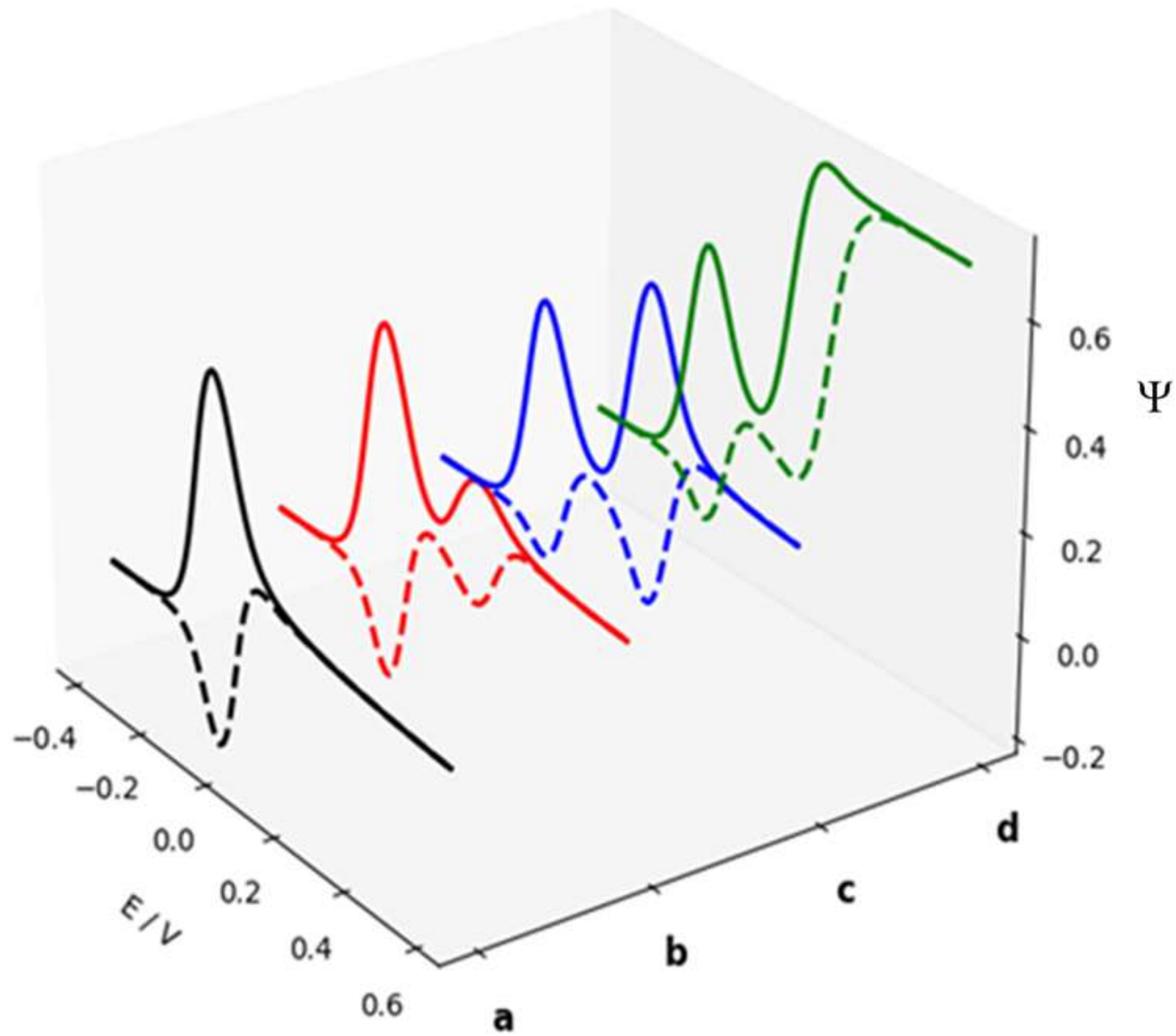
Simulations of the ECrevEC′ mechanism under conditions of Square-wave voltammetry (SWV) reveal rich and highly diagnostic features in both forward and backward current responses, allowing subtle mechanistic effects to be distinguished through peak shape, symmetry, peak separation, and current ratios. This makes the model particularly powerful for interpreting experimental voltammetric data in complex systems where multiple coupled chemical reactions coexist. The ECrevEC′ mechanism therefore serves as a versatile theoretical platform for studying, classifying, and rationalizing a broad spectrum of electrochemical processes, with direct applicability in redox catalysis, bio-electrochemistry, energy conversion systems, and mechanistic analysis of multistep electrode reactions. In the current work, we give all important figures, and the entire theoretical model in MATHCAD.

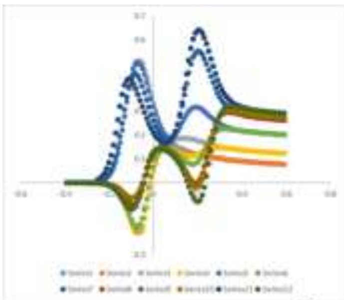
$$\mathbf{E}_1: \quad \mathrm{R} \underset{k_{s,1}^{-1}}{\overset{k_{s,1}}{\rightleftharpoons}} \mathrm{Ox} + e^-$$

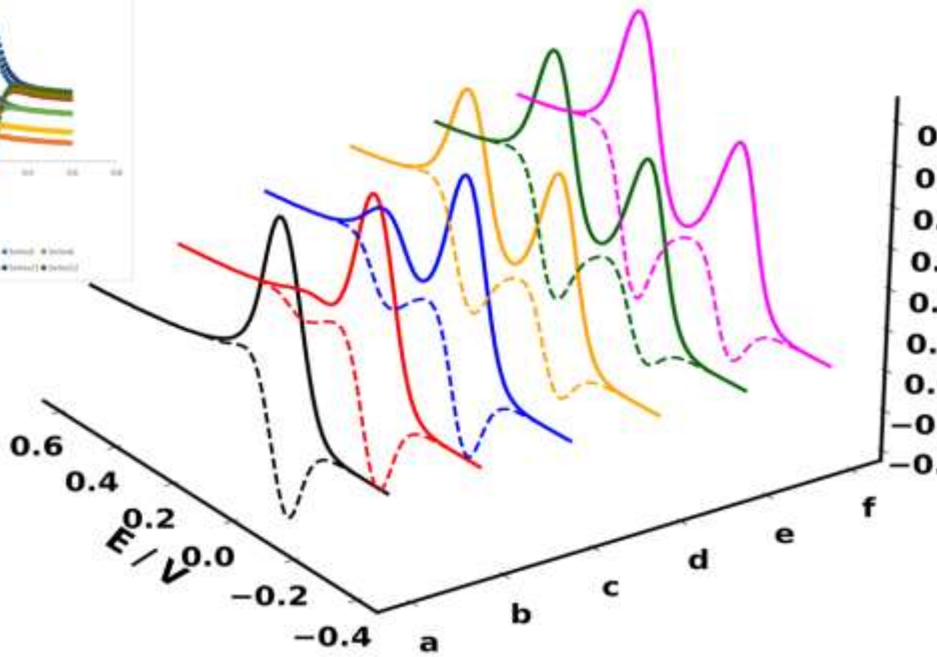
$$\mathbf{C}_{\mathrm{rev}}: \quad \mathrm{Ox} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Int} \qquad (K_{\mathrm{eq}} = k_f/k_b)$$

$$\mathbf{E}_2: \quad \mathrm{Int} \underset{k_{s,2}^{-1}}{\overset{k_{s,2}}{\rightleftharpoons}} \mathrm{Red} + e^-$$

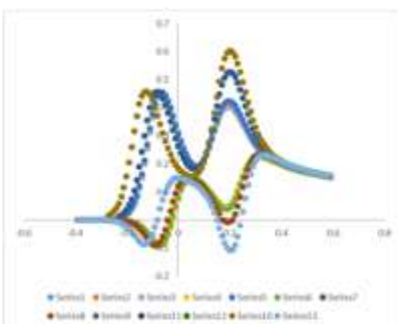
$$\mathbf{C}'\,(\mathrm{regenerative}): \quad \mathrm{Red} + \mathrm{Y} \xrightarrow{k_c} \mathrm{R}$$



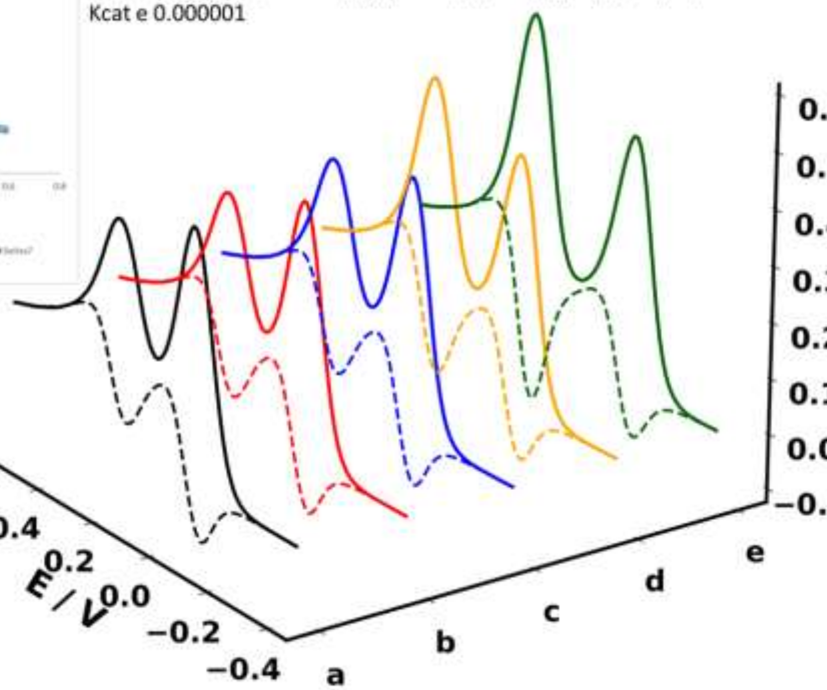


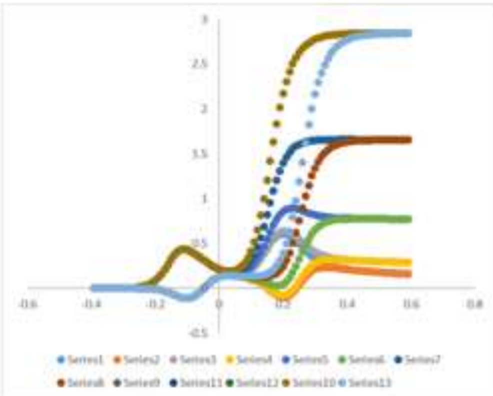


Nema kataliza
Kchem se menuva
Pri Keq od 0.5

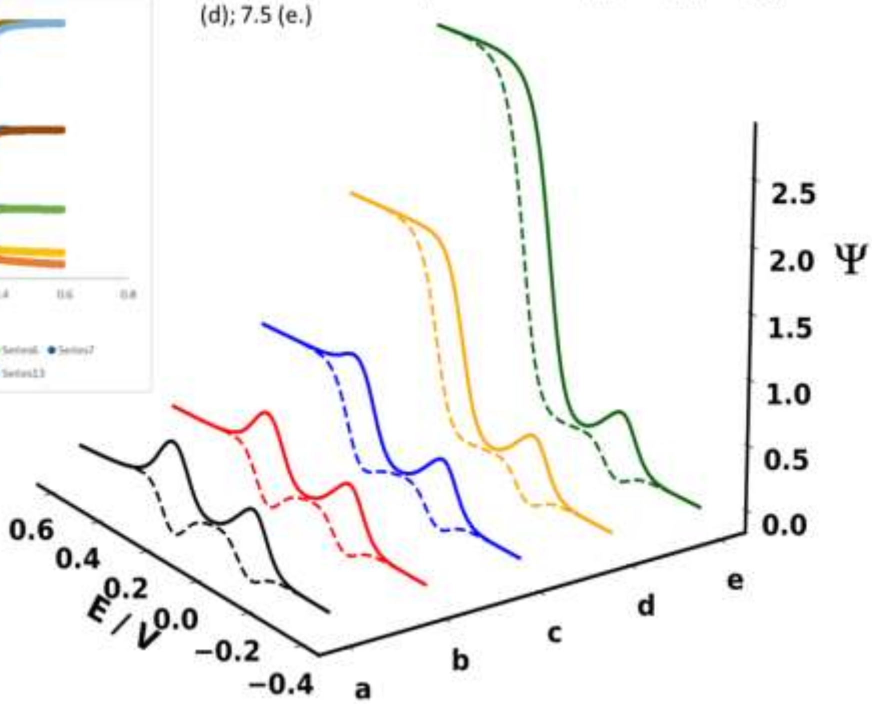


Kchem e 0.5; Keq = 0.001 (q), a; 0.01 (b); 0.1 (c,); 1 (d); 10 (e.).
Kcat e 0.000001



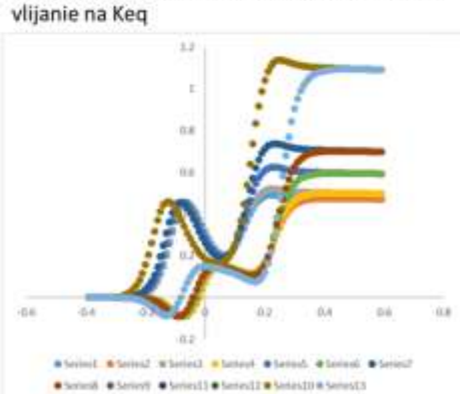


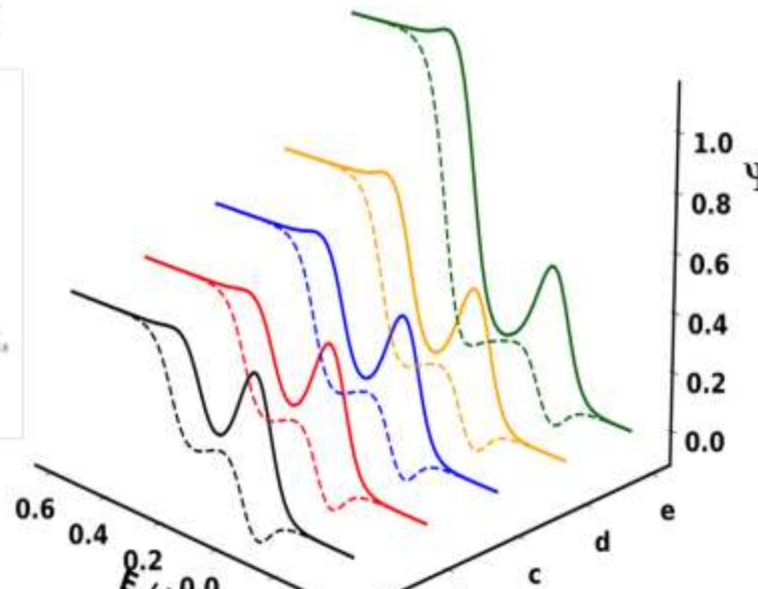
Keq = 1.1; Kchem = 10, a Kcat e 0.001 (a); 0.05 (b); 0.5 (c,); 2.5 (d); 7.5 (e.)



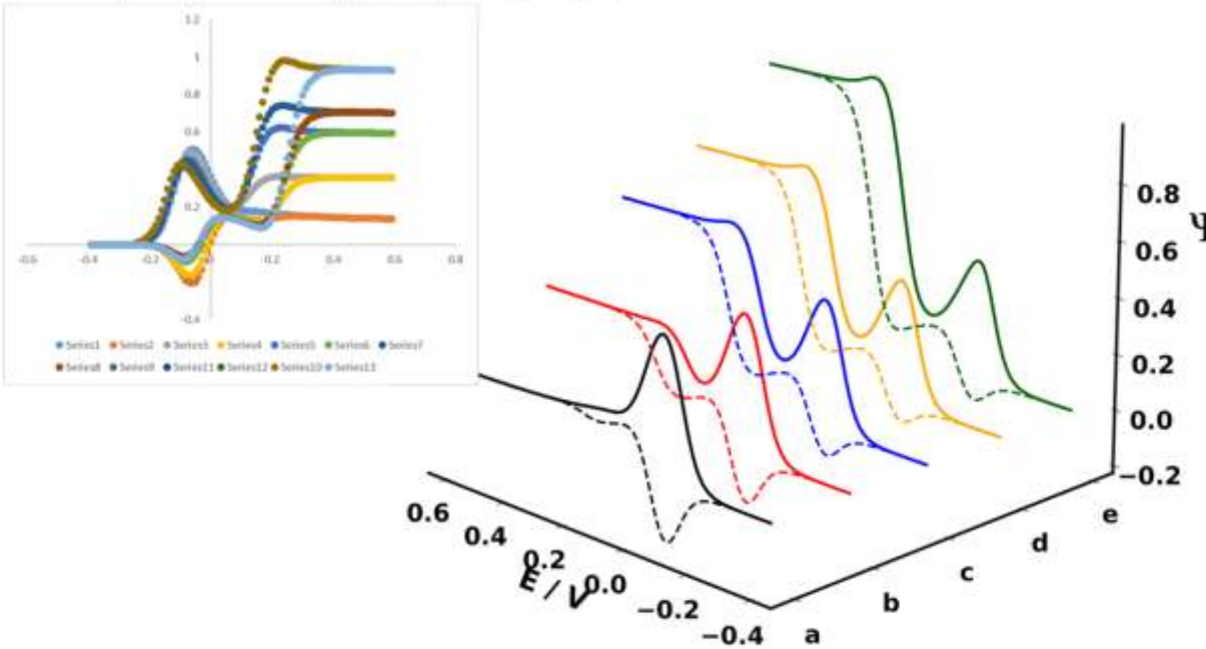
KI – KII = 5.61
Alpha e 0.5
Esw e 50 mV
dE e 10 mV
n e 1

Kchem e 0.5; Keq = 0.01 (q), a; 0.1 (b); 0.5 (c,)
Kcat e 1 . Ova e slika Pri umerena kataliza i um
vlijanie na Keq

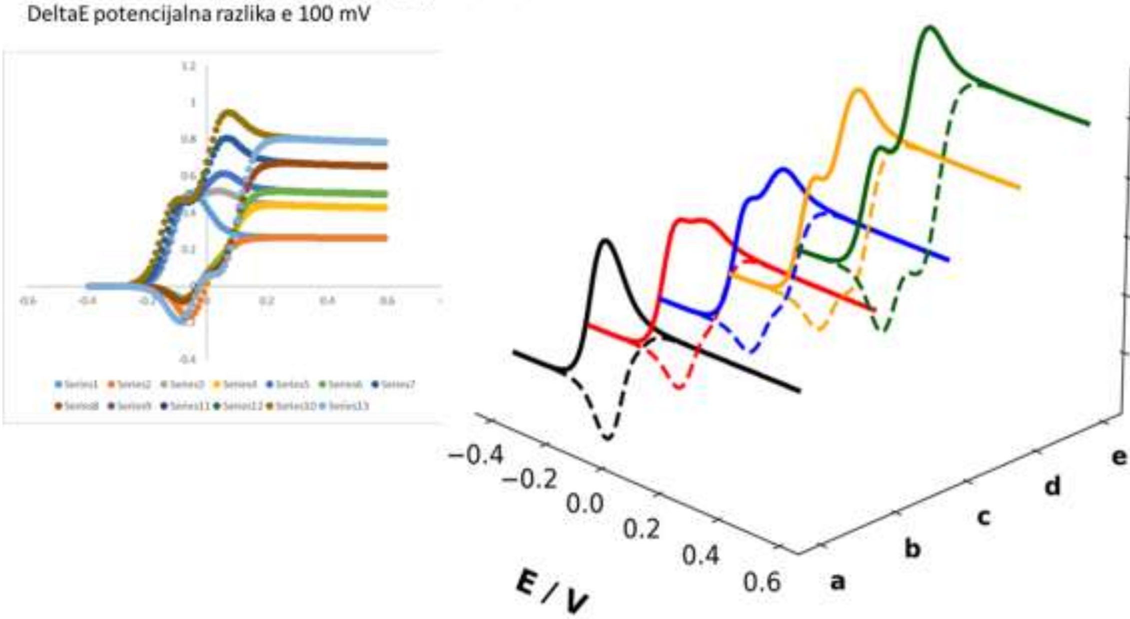




Keq e 0.5; Kchem = 0.01 (q), a; 0.1 (b); 0.5 (c,); 1 (d); 5 (e.). Kcat e 1



Keq e 0.5; Kchem = 0.1 (q), a; 0.5 (b); 1 (c,); 5 (d); 50 (e.). Kcat e 1
DeltaE potencijalna razlika e 100 mV



TWO STEP DIFFUSIONAL ECrevEC'cat Mechanism in SWV--new version proveren 23 12 2025 OK tocen, solved in Porto 2007
Effect of SW frequency

$f := 10$

$EsI := -0.4 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := -0.7 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{.75 \cdot r} \quad KII := 10^{.75}$

$Keq := .1001$

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

$\alpha 2 := 0.5$

$Kchem := 50.00$

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

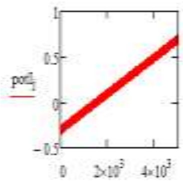
Kchem

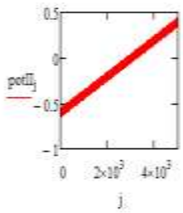
$$potI_j := (EsI + Esw) + \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$KI_1 = 5.623$

Kchem e kineticki parametar na reverzibilna intermediema hemiska reakcija

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





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

$z := .5000001$
z e kataliticki parametar
model povrzan so vtor cekor

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

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

$x := 0.001$

$S_j := \sqrt{j} - \sqrt{j-1}$

$$\Psi I_{1,r} := \frac{KI_r \cdot e^{\alpha 1 \cdot \Phi I_1}}{1 - KI_r \cdot e^{\alpha 1 \cdot \Phi I_1} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi I_1}}{1 + Keq}\right)\right) - \frac{KI_r \cdot e^{-\Phi I_1} \cdot A_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]}$$

$$\Psi II_{1,r} := \frac{KII \cdot \frac{1}{\sqrt{Kchem}} \cdot e^{\alpha 2 \cdot \Phi II_1}}{1 + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{\Phi II_1 \cdot \alpha 2} + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{-\Phi II_1 \cdot (1 - \alpha 2)}}$$

$\Psi I_{1,1} = 1.603 \times 10^{-6}$

$\Psi II_{1,1} = 9.108 \times 10^{-12}$

$$\Psi I_{j,r} = \frac{KI_r \cdot e^{\alpha 1 \cdot \Phi I_j}\left[1 - \frac{1}{\sqrt{50\pi}}\left(1+\frac{e^{-\Phi I_j}}{1+Keq}\right)\sum_{i=1}^{j-1}\left(\Psi I_{i,r} \cdot S_{j-i+1}\right) - \frac{KI_r \cdot e^{-\Phi I_j}}{(1+Keq)\sqrt{Kchem}}\sum_{i=1}^{j-1}\left(\Psi I_{i,r} \cdot A_{j-i+1}\right)\right]}{1 - KI_r \cdot e^{\alpha 1 \cdot \Phi I_j}\left[\frac{-2}{\sqrt{50\pi}}\left(\left(1+\frac{e^{-\Phi I_j}}{1+Keq}\right)\right) - \frac{KI_r \cdot e^{-\Phi I_j} \cdot A_1}{\sqrt{Kchem}\,(Keq+1)}\right]}$$

$$\Psi II_{j,r} = \frac{\frac{2KII}{\sqrt{50\cdot\pi}} \cdot 1 \cdot e^{\alpha 2 \cdot \Phi II_j}\sum_{i=1}^{j}\left(\Psi I_{i,r} \cdot S_{j-i+1}\right) - \frac{KII}{\left[(1+Keq)\cdot\sqrt{Kchem}\right]} e^{\alpha 2 \cdot \Phi II_j}\sum_{i=1}^{j}\left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - \frac{1}{(\sqrt{2})} KII \cdot e^{\Phi II_j \cdot \alpha 2}\sum_{i=1}^{j-1}\left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{2})} KII \cdot e^{-\Phi II_j \cdot (1-\alpha 2)}\sum_{i=1}^{j-1}\left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 - \frac{2KII}{\sqrt{50\cdot\pi}} \cdot 1 \cdot e^{\alpha 2 \cdot \Phi II_j} + \frac{KII}{\left[(1+Keq)\cdot\sqrt{Kchem}\right]} e^{\alpha 2 \cdot \Phi II_j} + \frac{1 \cdot B_1}{(\sqrt{2})} KII \cdot e^{\Phi II_j \cdot \alpha 2} + \frac{1 \cdot B_1}{(\sqrt{2})} KII \cdot e^{-\Phi II_j \cdot (1-\alpha 2)}}$$

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

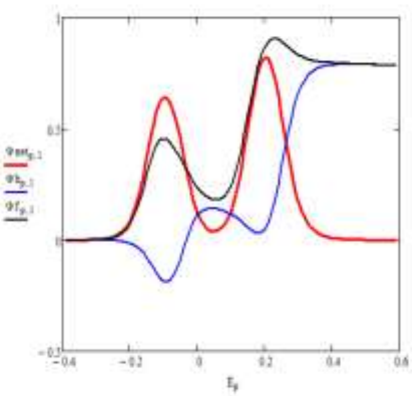
$$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$$

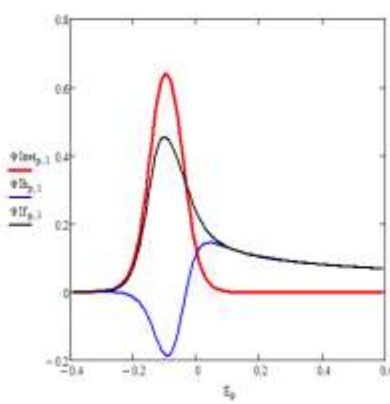
$$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r} \quad \Psi Ib_{p,r} := \Psi I_{50\cdot p+2,r} \quad \Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$$

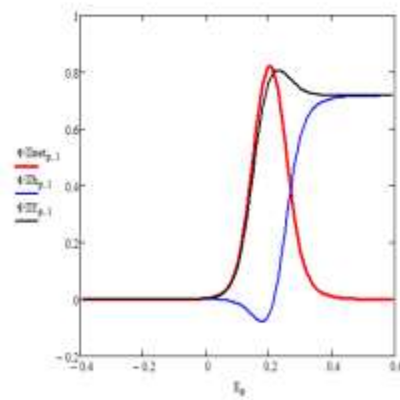
$$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r} \quad \Psi IIf_{p,r} := \Psi II_{(p+1)\cdot} \quad \Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$$

$$E_p := Eal + p \cdot dE$$

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







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