Theoretical Aspects of Diffusional Two Step Electrochemical Mechanism Associated with Regenerative Reaction to First Electrochemical Step and Follow Up Reversible Chemical Reaction Linked to the Product of Second Electrochemical Step

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MATHCAD WORKING FILE for Diffusional EC'ECrev Mechanism in Square-wave Voltammetry

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.004 \quad Esw := 0.05 \quad EsII := 0.7 \quad r := 1..1$

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

$KII := 10^{1}$

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

$\log(KI_r) =$ 1

TWO STEP DIFFUSIONAL EC'ECrev Mechanism in SWV---
this is EE diffusional mechanism with regenerative irreversible reaction associated with the product of first electrode transformation and reversible follow up chemical reaction associated with the product of the second electron transfer step

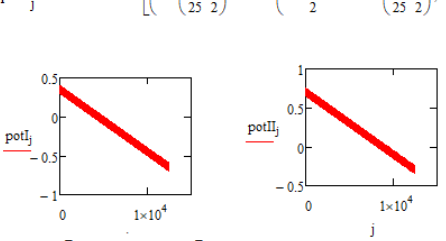
$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$

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

$\lambda := 10.0000000001000$

λ e hemiski kataliticki parametar

$KI_1 = 10$



$+Y$

$A + 1e{=}B{+}1e{=}C \quad +K = D$

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

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

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

$z := 1$

z e hem parametar na follow up

L e konst na ramnoteza na hem follow up

$L := 1000$

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

$x := 0.001$

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

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

$\Psi I_{1,1} = 1.151\times 10^{-5}$

$\Psi II_{1,1} = 1.308\times 10^{-12}$

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

$$\Psi II_{j,r} := \frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right) - KII\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right) - \frac{2}{\sqrt{\pi\cdot 50}}\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right) - \frac{L}{(\sqrt{z})\cdot(1+L)}KII\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right)}{1 + KII\cdot\frac{2\cdot M1_1}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1 + e^{\Phi II_j}\right) + \frac{2B_1}{\sqrt{\pi\cdot 50}}\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)} + \frac{LB_1}{\sqrt{z}}\frac{KII}{1+L}\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}}$$

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

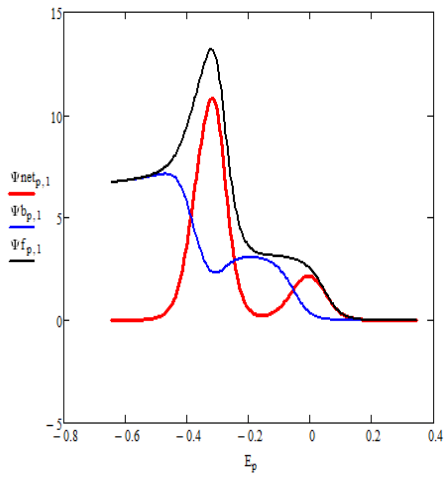
$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$

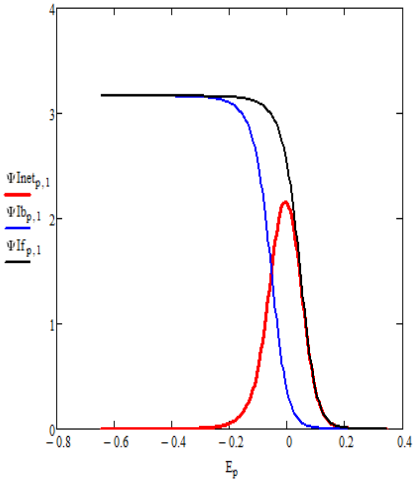
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

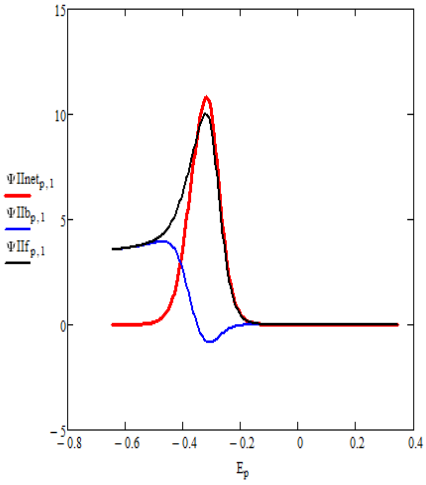
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

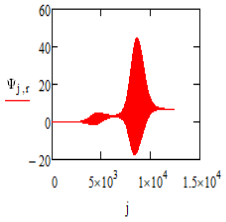
$E_p := EsI - p\cdot dE$

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









$\Psi f_{p,1} =$

$3.654\cdot10^{-5}$
$4.269\cdot10^{-5}$
$4.988\cdot10^{-5}$
$5.828\cdot10^{-5}$
$6.809\cdot10^{-5}$

$\Psi b_{p,1} =$

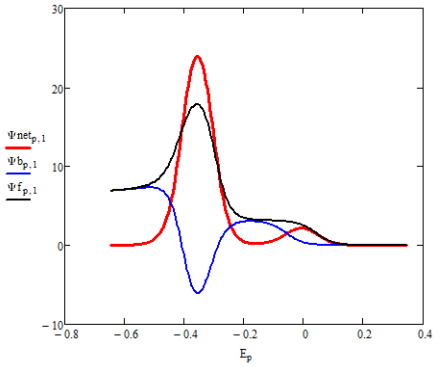
$7.401\cdot10^{-7}$
$8.648\cdot10^{-7}$
$1.011\cdot10^{-6}$
$1.181\cdot10^{-6}$
$1.38\cdot10^{-6}$
$1.612\cdot10^{-6}$

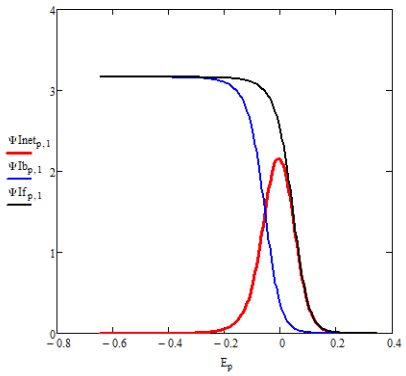
$\Psi net_{p,1} =$

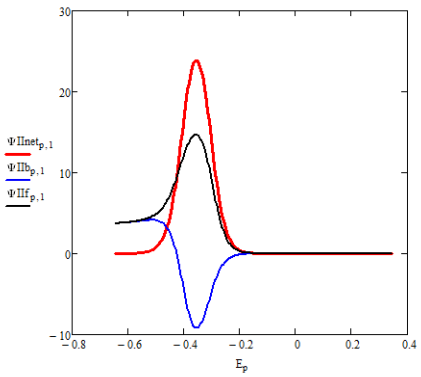
$3.064\cdot10^{-5}$
$3.58\cdot10^{-5}$
$4.183\cdot10^{-5}$
$4.887\cdot10^{-5}$
$5.71\cdot10^{-5}$

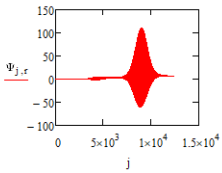
$E_p =$

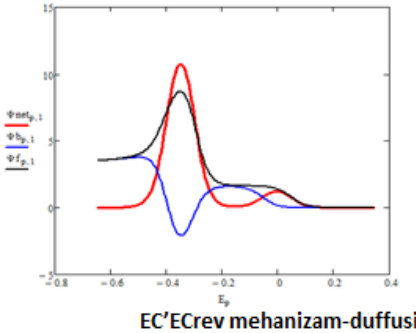
0.342
0.338
0.334
0.33
0.326

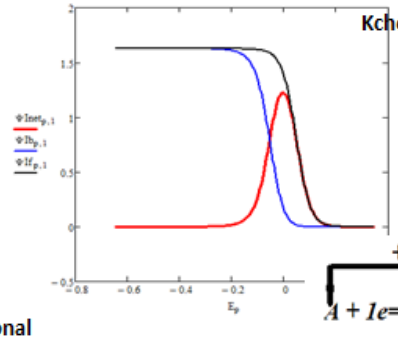




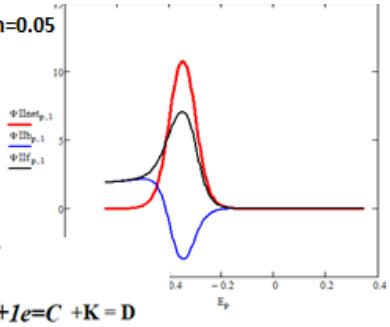








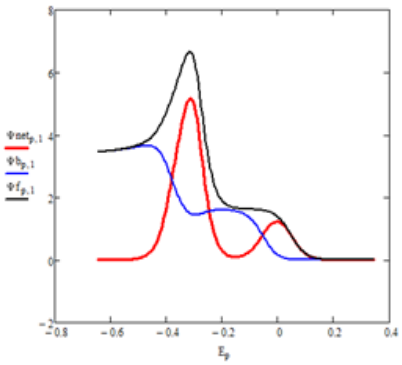
Kchem=0.05

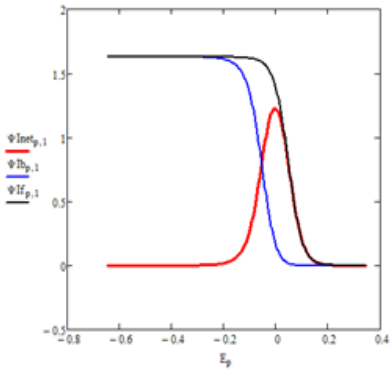


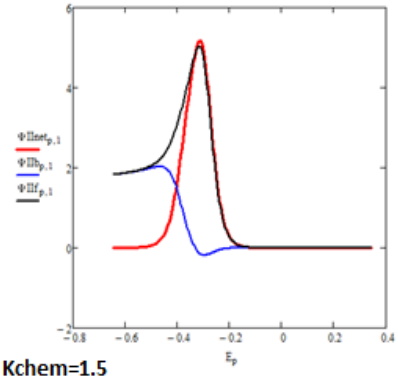
$$A + 1e = B + 1e = C \xrightarrow{+Y} +K = D$$

EC'ECrev mehanizam-duffusional

Kcat = 2.65: Ket,1=Ket,2=10; ; Keq=1000, vlijanie na Kchem, alpha e 0.5; dE =4 mV; Esw = 50 mV

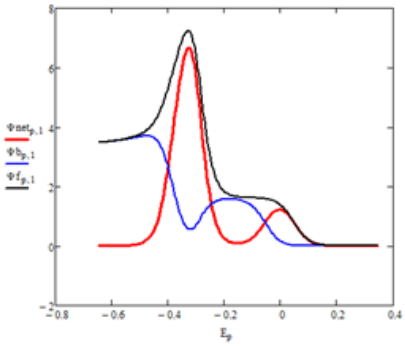


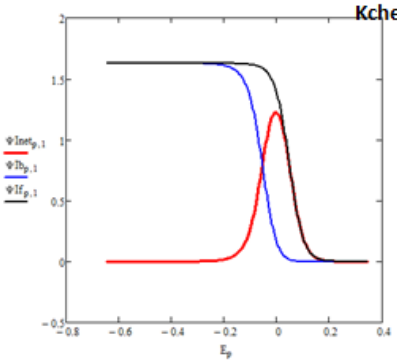


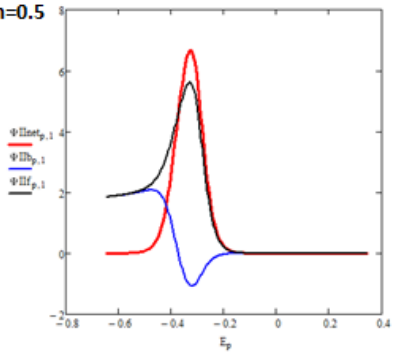


Kchem=1.5

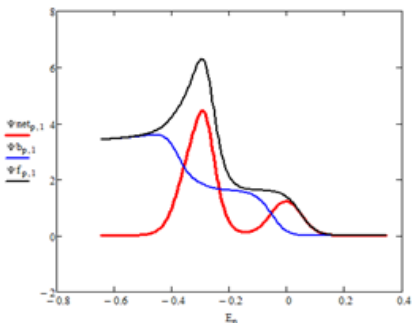
Kchem=0.5

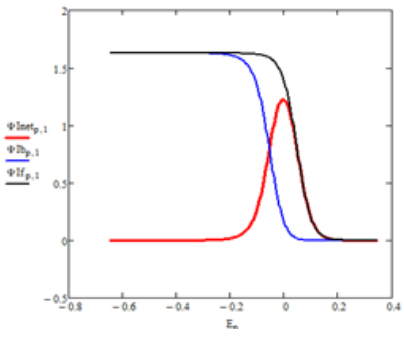


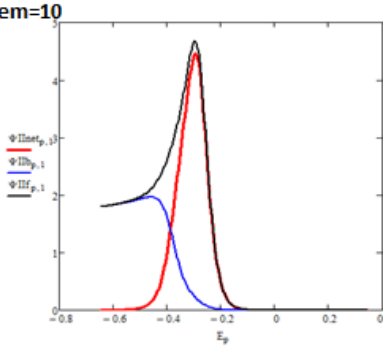


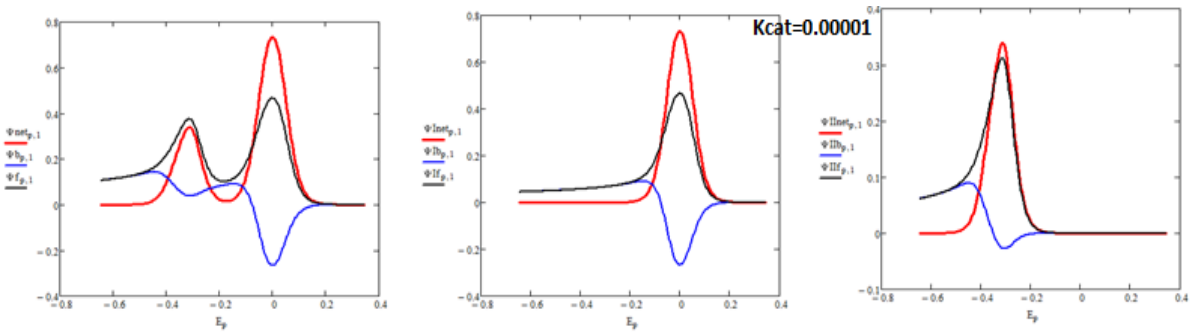


Kchem=10



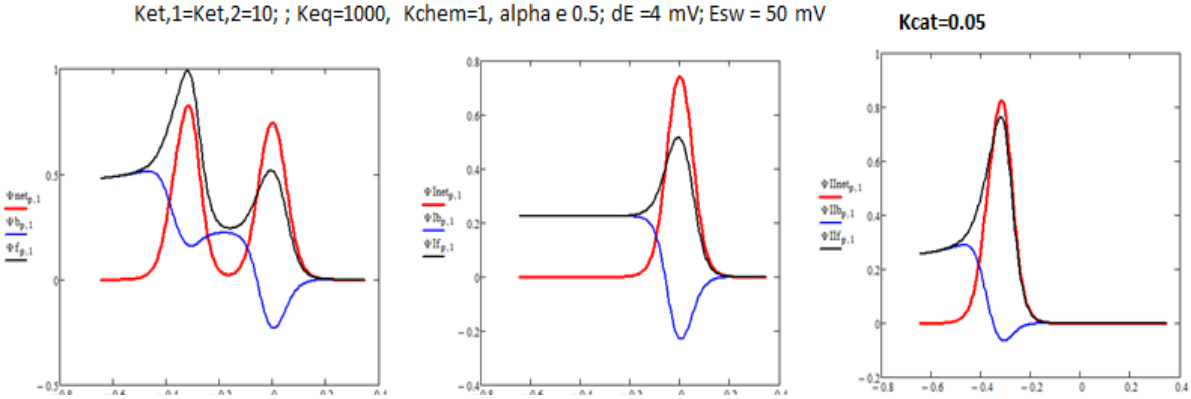


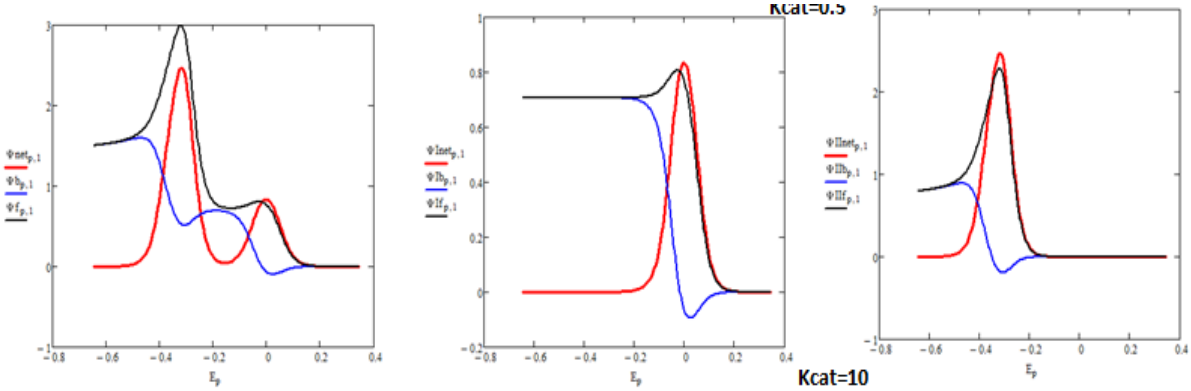


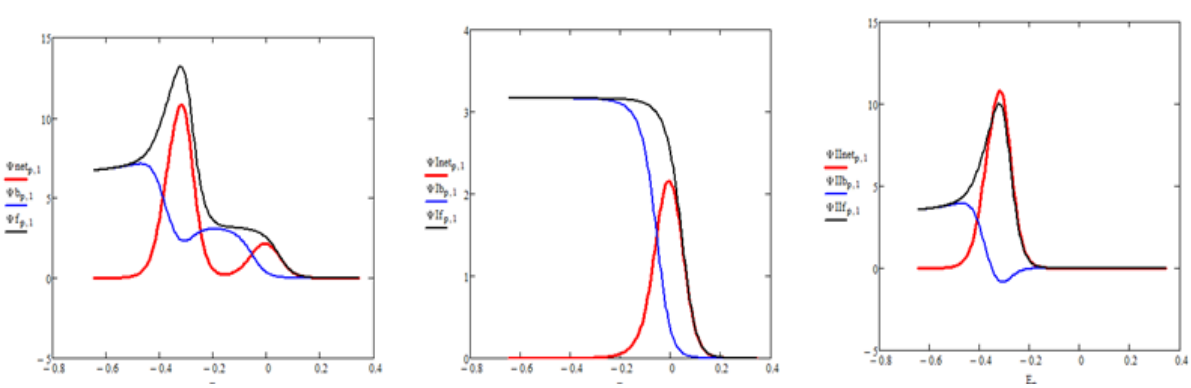


EC'Ecrev mehanizam-Vlijanie na Kcat

Ket,1=Ket,2=10; ; Keq=1000, Kchem=1, alpha e 0.5; dE =4 mV; Esw = 50 mV







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