

# MATCAD platform for calculating cyclic voltammograms

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## Abstract:

A practical on-line MATHCAD simulation platform, which can be used to calculate cyclic voltammograms of simple Red -1e- = Ox mechanism, is presented. The platform is free to use for everyone. In a series of such simulation platforms, we gonna provide all MATHCAD files needed to calculate cyclic voltammograms of all relevant electrochemical mechanisms.

$$E_s = -0.4 \quad E_f = 0.4 \quad \Delta E = E_f - E_s \quad dE = 0.004 \quad \tau = 0.01 \quad d = \frac{\tau}{25}$$

$$m = \frac{t_{oc}}{d} + 1 \cdot \frac{\Delta E}{dE} \cdot 25 + \frac{t_{oc}}{d} \quad n = \frac{\Delta E}{dE} \cdot 25 + \frac{t_{oc}}{d} + 1 \cdot \left( \frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{t_{oc}}{d} \right)$$

$$E_m = E_s + \left[ \cos \left( \frac{m - \frac{t_{oc}}{d}}{25} \right) \cdot dE - dE \right]$$

$$E_a = E_f - \left[ \cos \left( \frac{n - \left( \frac{\Delta E}{dE} \cdot 25 + \frac{t_{oc}}{d} \right)}{25} \right) \cdot dE - dE \right]$$

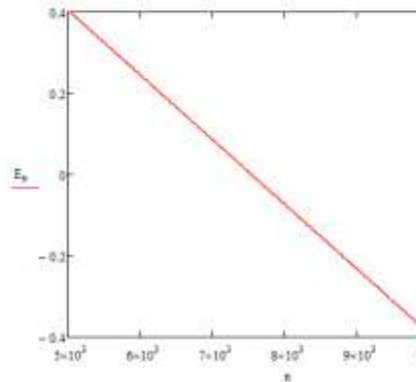
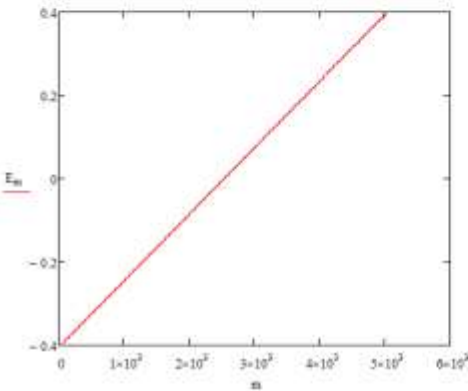
$$\lambda = 1 \cdot \frac{t_{oc}}{d}$$

$$\frac{\Delta E}{dE} = 200$$

ECrev Diffusional Mechanism  
in Cyclic Voltammetry

WHEN Equilibrium Constant  $M > 1000$ , mechanism converges to simple Red-1e- = Ox Mechanism

$\lambda$  is dimensionless kinetic parameter related to electrode reaction  
 $\gamma$  is dimensionless catalytic parameter related to preceding chemical reaction  
 $\alpha$  is electron transfer coefficient  
 $M$  is equilibrium constant of preceding chemical reaction  
 $k_f$  and  $k_b$  are forward and backward rate constants of preceding chemical reaction  
 $E_s$  is starting potential  
 $E_f$  is final potential  
 $dE$  is potential step  
 $\Psi$  is symbol for dimensionless current  
 $E_m$  is cathodic potential ramp in cyclic voltammetry  
 $E_a$  is anodic potential ramp  
 $Sk$  is integration factor  
 $\tau$  is duration of potential steps  
 $D$  is diffusion coefficient of Ox and Red



-0.396	-0.026
-0.392	-0.026
-0.388	-0.026
-0.384	-0.026
-0.38	-0.026
-0.376	-0.027
-0.372	-0.027
-0.368	-0.027
-0.364	-0.027
-0.36	-0.028
-0.356	-0.028
-0.352	-0.028
-0.348	-0.029
-0.344	-0.029
-0.34	-0.029
-0.336	-0.03
-0.332	-0.03
-0.328	-0.03
-0.324	-0.031
-0.32	-0.031
-0.316	-0.031
-0.312	-0.032
-0.308	-0.032
-0.304	-0.032
-0.3	-0.033
-0.296	-0.033
-0.292	-0.034
-0.288	-0.034
-0.284	-0.034
-0.28	-0.035
-0.276	-0.035
-0.272	-0.036
-0.268	-0.036
-0.264	-0.037
-0.26	-0.037
-0.256	-0.038

$$\lambda = 0.28 \quad \cos = 0.0000008$$

$$k_s = 0.005 \quad D = 3 \cdot 10^{-6} \quad k_f = 1.10 \quad 0.05 \quad 0$$

$$K_{eq} = \frac{k_f \sqrt{\tau}}{\sqrt{D}} \quad \alpha = 0.5 \quad k_b = 2.50010 \quad 0.075$$

$$M = \frac{k_f}{k_b} \quad \text{Konstanta na ramnoteza} \quad 0.35$$

$$\log(K) = -0.54 \quad K$$

$$\frac{M}{200} = 1.051000$$

$$E_s = 0.6590 \quad d = 2 \quad R = 8.314 \quad T = 298.15$$

$$\Phi_m = eI \frac{F}{R \cdot T} (E_m) \quad \Phi_a = eI \frac{F}{R \cdot T} (E_a)$$

$$\Phi_{ac} = dI \frac{F}{R \cdot T} E_s$$

$$\lambda = k_f + k_b \quad \text{kineticki parametar} \quad k = 1.2 \left( \frac{\Delta E}{dE} \cdot 25 + \frac{t_{oc}}{d} \right)$$

$$\tau = \tau \cdot \tau$$

$$Sl_k = \sqrt{\frac{k}{25}} - \sqrt{\frac{k-1}{25}} \quad Sl_s = a \quad z = (k_f + k_b)^{0.5} \cdot \tau$$

$$\gamma = b \cdot 1 \quad \gamma = 0.19$$

$$\Psi = K \cdot e^{-\alpha \Phi_1}$$

$$- \left[ 1 - \exp \left[ \sqrt{\frac{k-1}{25}} (k-1) \right] \right]$$

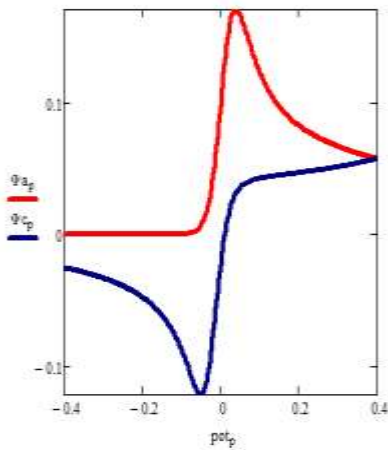
$$\psi_1 = \frac{K e^{\alpha \cdot \phi_1}}{1 + \frac{1 \cdot K e^{-(1-\alpha) \cdot \phi_1}}{\sqrt{\pi-1}} + \frac{1 \cdot K e^{-(1-\alpha) \cdot \phi_1}}{\sqrt{\pi-1}} \frac{M}{1+M} + \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot \phi_1} S_1}$$

$$\psi_s = \frac{K e^{\alpha \cdot \phi_{2s}} - \frac{2 \cdot K e^{\alpha \cdot \phi_{2s}}}{\sqrt{\pi-1}} \sum_{j=1}^{s-1} (\psi_j \cdot S1_{s-j+1}) - \frac{2 \cdot K e^{-(1-\alpha) \cdot \phi_{2s}}}{\sqrt{\pi-1}} \frac{M}{1+M} \sum_{j=1}^{s-1} (\psi_j \cdot S1_{s-j+1}) - \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot \phi_{2s}} \sum_{j=1}^{s-1} (\psi_j \cdot S_{s-j+1})}{1 + \frac{2 \cdot K e^{\alpha \cdot \phi_{2s}}}{\sqrt{\pi-1}} + \frac{2 \cdot K e^{-(1-\alpha) \cdot \phi_{2s}}}{\sqrt{\pi-1}} \frac{M}{1+M} + \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot \phi_{2s}} S_1}$$

$$\psi_m = \frac{K e^{\alpha \cdot \phi_m} - \frac{2 \cdot K e^{\alpha \cdot \phi_m}}{\sqrt{\pi-1}} \sum_{j=1}^{m-1} (\psi_j \cdot S1_{m-j+1}) - \frac{2 \cdot K e^{-(1-\alpha) \cdot \phi_m}}{\sqrt{\pi-1}} \frac{M}{1+M} \sum_{j=1}^{m-1} (\psi_j \cdot S1_{m-j+1}) - \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot \phi_m} \sum_{j=1}^{m-1} (\psi_j \cdot S_{m-j+1})}{1 + \frac{2 \cdot K e^{\alpha \cdot \phi_m}}{\sqrt{\pi-1}} + \frac{2 \cdot K e^{-(1-\alpha) \cdot \phi_m}}{\sqrt{\pi-1}} \frac{M}{1+M} + \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot \phi_m} S_1}$$

$$\psi_n = \frac{K e^{\alpha \cdot b_n} - \frac{2 \cdot K e^{\alpha \cdot b_n}}{\sqrt{\pi-1}} \sum_{j=1}^{n-1} (\psi_j \cdot S1_{n-j+1}) - \frac{2 \cdot K e^{-(1-\alpha) \cdot b_n}}{\sqrt{\pi-1}} \frac{M}{1+M} \sum_{j=1}^{n-1} (\psi_j \cdot S1_{n-j+1}) - \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot b_n} \sum_{j=1}^{n-1} (\psi_j \cdot S_{n-j+1})}{1 + \frac{2 \cdot K e^{\alpha \cdot b_n}}{\sqrt{\pi-1}} + \frac{2 \cdot K e^{-(1-\alpha) \cdot b_n}}{\sqrt{\pi-1}} \frac{M}{1+M} + \frac{\gamma}{1+M} e^{-(1-\alpha) \cdot b_n} S_1}$$

$$p = 1 - \frac{\Delta E}{dE} \quad \psi_{a_p} = (\psi) \left( \frac{\tau}{d \cdot 25} + p \right) \cdot 25 \quad \psi_{c_p} = (\psi) \left[ \frac{\Delta E}{dE} \cdot 2 + \left( \frac{\tau}{25 \cdot d} \right) \cdot p \right] \cdot 25 \quad \text{pot}_p = Es + p \cdot dE$$



-0.26	-0.037
-0.256	-0.038
-0.252	-0.038
-0.248	-0.039
-0.244	-0.039
-0.24	-0.04
-0.236	-0.04
-0.232	-0.041
-0.228	-0.042
-0.224	-0.042
-0.22	-0.043
-0.216	-0.044
-0.212	-0.044
-0.208	-0.045
-0.204	-0.046
-0.2	-0.047
-0.196	-0.047
-0.192	-0.048
-0.188	-0.049
-0.184	-0.05
-0.18	-0.051
-0.176	-0.052
-0.172	-0.053
-0.168	-0.054
-0.164	-0.055
-0.16	-0.056
-0.156	-0.058
-0.152	-0.059
-0.148	-0.06
-0.144	-0.062
-0.14	-0.063
-0.136	-0.065
-0.132	-0.066
-0.128	-0.068
-0.124	-0.07
-0.12	-0.072
-0.116	-0.074
-0.112	-0.076
-0.108	-0.079
-0.104	-0.081
-0.1	-0.084
-0.096	-0.087
-0.092	-0.09
-0.088	-0.093
-0.084	-0.096
-0.08	-0.1
-0.076	-0.103
-0.072	-0.107
-0.068	-0.11
-0.064	-0.113
-0.06	-0.116
-0.056	-0.119

silon =K/25{

$\psi_{c_p} =$

$$i_{c_p} = \Phi_{c_p} F A 0.446 \sqrt{D} \frac{0.001}{\sqrt{t}}$$

$$i_{a_p} = \Phi_{a_p} F A 0.446 \sqrt{D} \frac{0.001}{\sqrt{t}}$$

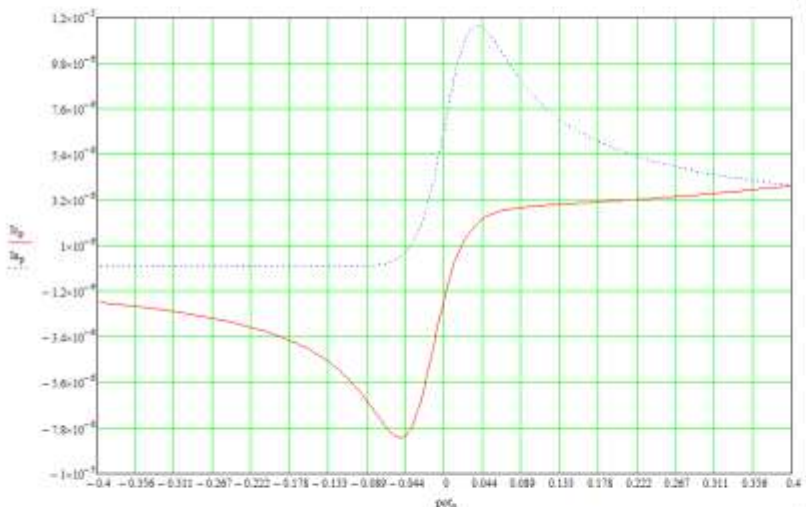
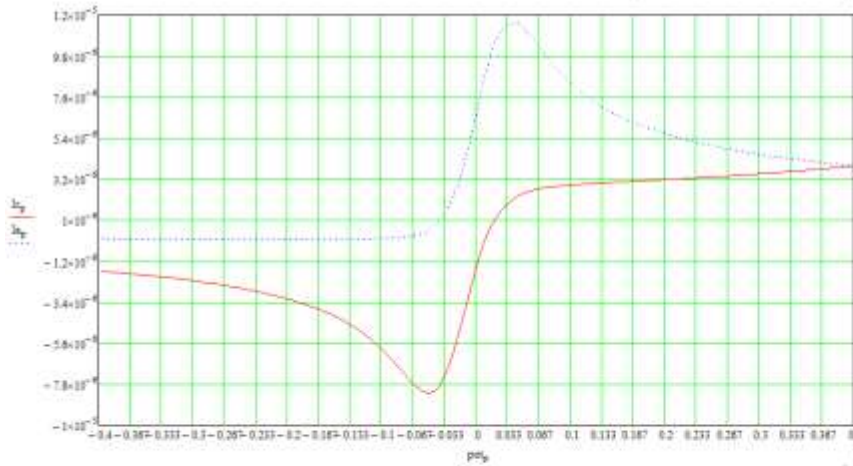
$$R_a = 10000$$

$$pot_p = E_a + p \cdot dE - (i_{c_p} - i_{a_p}) R_a$$

$$\frac{1}{\sqrt{t}} - 1 = -4$$

$pot_p =$	$-8 \times 10^{-3}$
	$-4 \times 10^{-3}$
	0
	$4 \times 10^{-3}$
	$8 \times 10^{-3}$
	0.012
	0.016
	0.02
	0.024
	0.028
	0.032
	0.036
	0.039
	0.042
	0.045
	0.048
	0.051
	0.054
	0.057
	0.06
	0.064
	0.068
	0.072
	0.076
	0.08
	0.084
	0.088
	0.092
	0.096
	0.1
	0.104
	0.108
	0.112
	0.116
	0.12
	0.124
	0.128
	0.132
	0.136
	0.14
	0.144
	0.148
	0.152
	0.156
	0.16
	0.164
	0.168
	0.172
	0.176
	0.18
	0.184
	0.188
	0.192
	0.196
	0.2
	0.204
	0.208
	0.212
	0.216
	0.22
	0.224
	0.228
	0.232
	0.236
	0.24
	0.244
	0.248
	0.252
	0.256
	0.26
	0.264
	0.268
	0.272
	0.276
	0.28
	0.284
	0.288
	0.292
	0.296
	0.3

$\Phi_{c_p} =$	-0.033
	-0.044
	-0.055
	-0.023
	-0.013
	$-0.017 \times 10^{-3}$
	$2.426 \times 10^{-3}$
	$8.882 \times 10^{-3}$
	0.014
	0.019
	0.023
	0.026
	0.029
	0.031
	0.033
	0.035
	0.037
	0.039
	0.041
	0.042
	0.043
	0.044
	0.045
	0.046
	0.047
	0.048
	0.049
	0.05
	0.051
	0.052
	0.053
	0.054
	0.055
	0.056
	0.057
	0.058
	0.059
	0.06
	0.061
	0.062
	0.063
	0.064
	0.065
	0.066
	0.067
	0.068
	0.069
	0.07
	0.071
	0.072
	0.073
	0.074
	0.075
	0.076
	0.077
	0.078
	0.079
	0.08
	0.081
	0.082
	0.083
	0.084
	0.085
	0.086
	0.087
	0.088
	0.089
	0.09
	0.091
	0.092
	0.093
	0.094
	0.095
	0.096
	0.097
	0.098
	0.099
	0.1



$$4.5 \frac{100}{2.13} = 209.302$$

$$pot_p = \quad i_{c_p} = \quad i_{a_p} =$$

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