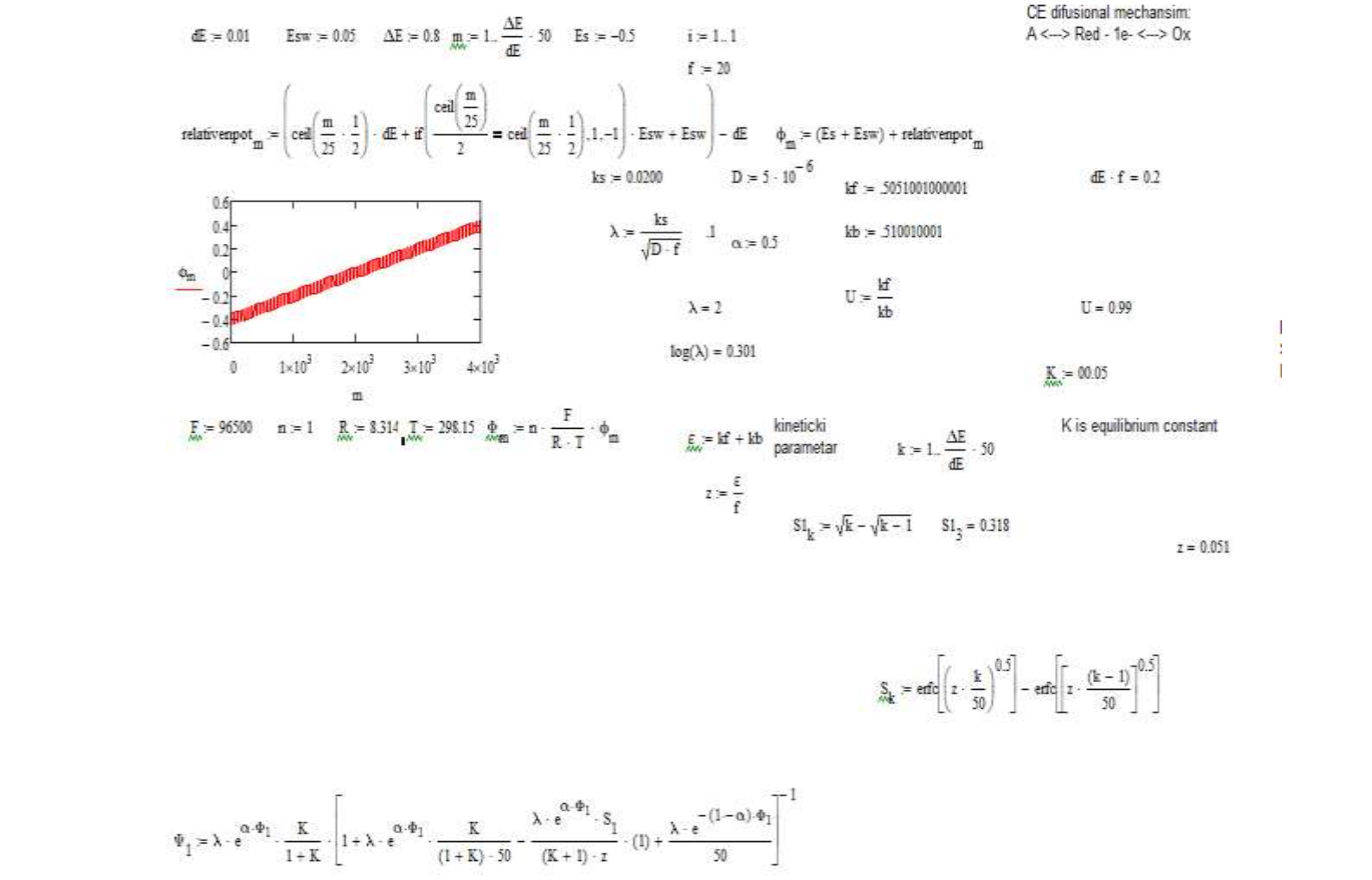
Effect of Equilibrium Constant of Chemical Reaction to the features of square-wave voltammograms of a diffusional "CrevErev" mechanism featuring preceding homogeneous chemical step

Rubin Gulaboski

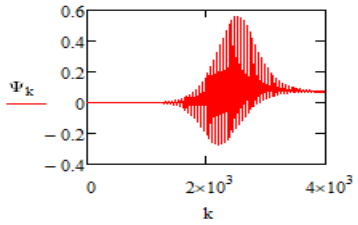
Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract: The electrochemical diffusional mechanism featuring reversible homogeneous chemical reaction (diffusional :"CrevErev" mechanism) is solved theoretically under conditions of square-wave voltammetry. In this file, a MATHCAD simulation protocol of this important electrochemical mechanism is presented, while highlighting the effect of equilibrium constant of the chemical step to the features of all current components of simulated Square-wave voltammograms. Method for the determination of equilibrium constant (Keq) is proposed. MATHCAD file provided is free and ready to use.



$$\Psi_k := \frac{\frac{\lambda \cdot e^{\alpha \cdot \Phi_k} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{50 \cdot \pi}} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S1_{k-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{\alpha \cdot \Phi_k} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S_{k-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{-\Phi_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S1_{k-j+1}\right)}{\left(\frac{\lambda \cdot e^{\alpha \cdot \Phi_k} \cdot K}{1+K} \cdot \frac{2 \cdot S1_1}{\sqrt{50 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{\alpha \cdot \Phi_k} + \lambda \cdot \frac{2 \cdot S1_1}{\sqrt{50 \cdot \pi}} \cdot e^{-\Phi_k \cdot (1-\alpha)}}$$

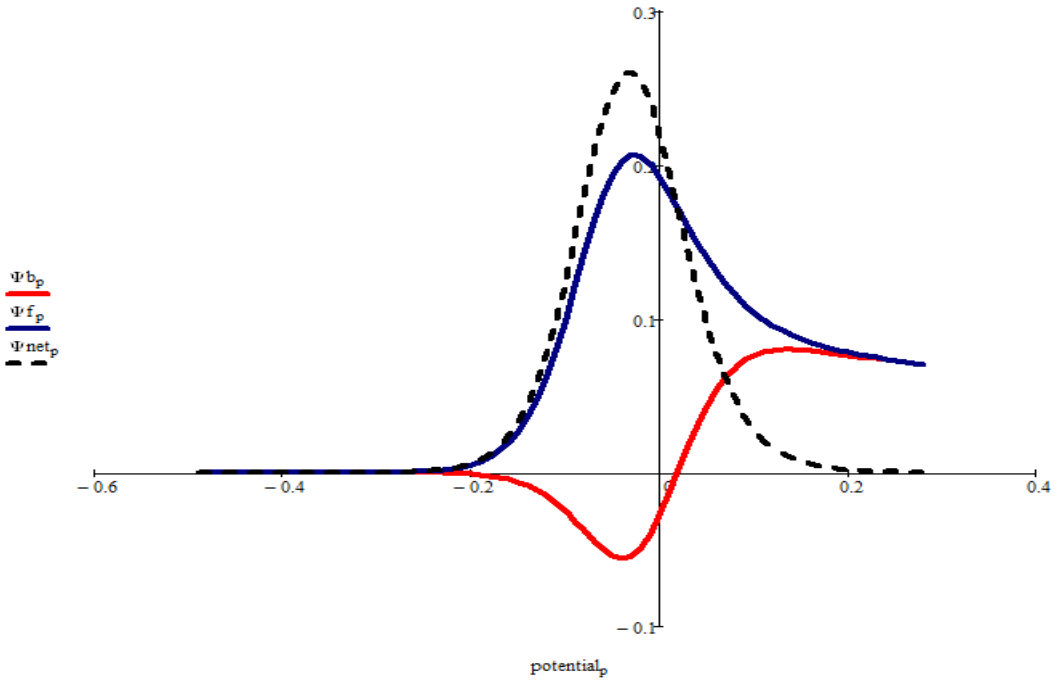
$\Psi_1 =$ -



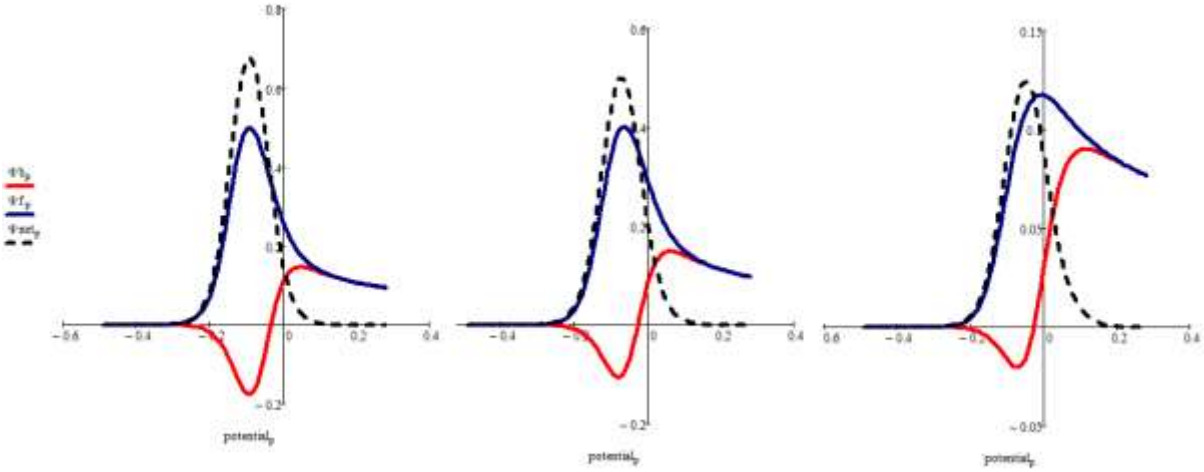
$\Psi_{k,i} =$

$p := 1 .. \frac{\Delta E}{dE} - 2$ $\quad \Psi f_p := (\Psi)_{(p+1)\cdot 50}$ $\quad \Psi b_p := (\Psi)_{50 \cdot p + 25}$

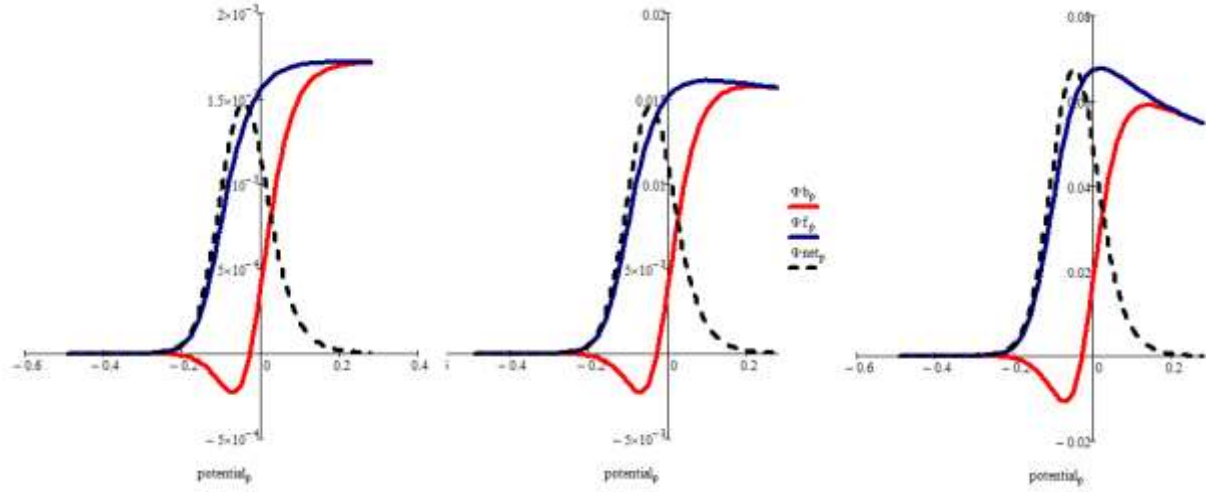
$\Psi net_p := \Psi f_p - \Psi b_p$ $\quad potential_p := Es + (p) \cdot dE$



6.747 × 10⁻
9.253 × 10⁻
1.33 × 10⁻
1.94 × 10⁻
2.848 × 10⁻
4.192 × 10⁻
6.179 × 10⁻
9.113 × 10⁻
1.344 × 10⁻
1.984 × 10⁻
2.928 × 10⁻
4.322 × 10⁻
6.38 × 10⁻
9.418 × 10⁻
1.39 × 10⁻
2.052 × 10⁻
3.03 × 10⁻
4.474 × 10⁻
6.605 × 10⁻
9.751 × 10⁻
1.44 × 10⁻
2.125 × 10⁻
3.137 × 10⁻
4.628 × 10⁻
6.825 × 10⁻
1.006 × 10⁻
1.48 × 10⁻



Effect of equilibrium constant of preceding chemical reaction the features of simulated square-wave voltammograms of a CErev mechanism at high rates of chemical step. SW voltammograms are calculated for Keq = 5.5; 0.5 and 0.05 (from left to right)



Effect of equilibrium constant of preceding chemical reaction the features of simulated square-wave voltammograms of a CErev mechanism at high rates of chemical step and low values of Keq. SW voltammograms are calculated for Keq = 0.00005; 0.0005 and 0.025 (from left to right)

LITERATURE

1. R. Gulaboski, ***Journal of Solid State Electrochemistry*** 24 (**2020**) 2081-2081
2. R. Gulaboski, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, ***Journal of Physical Chemistry C*** 112 (2008) 153-161
3. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, ***Electrochemistry Communications*** 7 (2005) 515-522.
4. R Gulaboski, V Mirceski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 39 (2020) 153-166
5. V. Mirceski, R. Gulaboski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 33 (2014), 1-12
6. V. Mirceski, R. Gulaboski, ***Journal of Solid State Electrochemistry*** 7 (2003) 157-165
7. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, ***Electroanalysis*** 31 (2019) 2488-2506
8. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842
9. R. Gulaboski, C.M. Pereira, M.N.D.S Cordeiro, I. Bogeski, F. Silva, ***Journal of Solid State Electrochemistry,*** 9, **2005**, 469-474
10. B. Sefer, R. Gulaboski, V. Mirceski, ***Journal of Solid State Electrochemistry*** 16 (2012) 2373-2381.
11. V. Mirceski, R. Gulaboski, ***Bulletin of the Chemists and Technologists of Macedonia*** 18 (1999) 57-64.
12. R. Gulaboski, C. M. Pereira, ***Electroanalytical Techniques and Instrumentation in Food Analysis***; in Handbook of Food Analysis Instruments (2008) 379-402.
13. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, ***Journal of Physical Chemistry B*** 110 (2006) 12530-12538.
14. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, ***Analytical Chemistry*** 91 (2019) 14904-14910.
15. V. Mirceski, R. Gulaboski, F. Scholz, ***Journal of Electroanalytical Chemistry*** 566 (2004) 351-360.

16. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435

17. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842

18. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621

19. R. Gulaboski, V. Mirceski, F. Scholz, ***Amino Acids*** 24 (2003) 149-154

20. V. Mirceski, R. Gulaboski, ***Croatica Chemica Acta*** 76 (2003) 37-48.

21. F. Scholz, R. Gulaboski, ***Faraday Discussions*** 129 (2005) 169-177.

22. R. Gulaboski, K. Caban. Z. Stojek, F. Scholz, ***Electrochemistry Communications*** 6 (2004) 215-218.

23. V. Mirceski, R. Gulaboski, ***Journal of Physical Chemistry B***, 110 (2006) 2812-2820.

24. V. Mirceski, R. Gulaboski, B. Jordanoski, S. Komorsky-Lovric, ***Journal of Electroanalytical Chemistry,*** 490 (2000) 37-47.

25. R. Gulaboski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 41 (2022) 151-162

26. R. Gulaboski, P. Kokoskarova, S. Petkovska, ***Analytical&Bioanalytical Electrochemistry***, 12 (2020) 345-364.

27. V. Mirčeski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (10) **2002**, 814-819

28. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S Cordeiro, ***Molecular Physics*** 104 (2006) 3627-3634.

29. R. Gulaboski, V. Mirceski, M. Lovric, ***Macedonian Journal of Chemistry and Chemical Engineering*** 40 (2021) 1-9.

30. R. Gulaboski, P. Kokoskarova, S. Risafova, ***J. Electroanal. Chem***. 868 (2020) 114189.

31. R. Gulaboski, V. Mirceski, ***Journal of Solid State Electrochemistry*** 28 (2024) 1121-1130.

32. V. Mirceski, B. Mitrova, V. Ivanovski, N. MItreska, A. Aleksovska, R. Gulaboski, ***Journal of Solid State Electrochemistry*** 19 (2015) 1121-1130.

33. I. Spirevska, L. Soptrajanova, R. Gulaboski, **Analytical Letters** 33 (2000) 919-928.