EDUCATIONAL VOLTAMMETRY: PART 2: Open Interactive Protocol to Simulate the CE Mechanism in Cyclic Staircase Voltammetry

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Abstract

For the first time, an open and freely accessible simulation platform based on MATHCAD is introduced for educational purposes in electrochemistry. This work, *Educational Voltammetry: Part 2*, provides interactive step-by-step protocols that enable students, educators, and researchers to simulate cyclic staircase voltammograms of a diffusional **CE(reversible)** electrode mechanism under a variety of experimental and kinetic conditions. The approach is designed both for learning and for practical training, making it possible to explore the effects of mass transfer, electrode kinetics, and a preceding homogeneous chemical step without requiring advanced programming skills. Upon request, the original MATHCAD files can be obtained directly from the authors. In forthcoming contributions to this series, free interactive protocols for additional important electrode mechanisms will be provided, further broadening the educational toolkit for voltammetric analysis. A 30-day free trial version of MATHCAD 15 is available at: https://support.ptc.com/products/Mathcad/Mathcad-15-0/free-trial?refid=cadventure

This initiative aims to encourage wider adoption of theoretical modeling in electrochemical education and to provide experimentalists with freely available tools for mechanistic understanding.

https://support.ptc.com/products/Mathcad/Mathcad-15-0/free-trial?refid=cadventure.

Supplementary: pdf version of File 1. MATHCAD simulation protocol of CrevE mechanism

$\mathrm{C_{rev}E}$ electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircase Voltammetry

$$\mathrm{Y = Red} \qquad (k_f, k_b, K_{eq}) \qquad (1)$$

$$\mathrm{Red = Ox + e^-} \qquad (k_s, \alpha) \qquad (2)$$

$Es := -0.5$ starting potential (in V vs. the formal potential)

$Ef := 0.5$ switching potential (in V vs. the formal potential)

$dE := 0.005$ potential step increment (in V)

$\Delta E := Ef - Es$ potential window

$v := 0.1$ potential scan rate in V/s

$\tau := \frac{dE}{v}$ duartion of a single step (in s)

$\tau = 0.05$

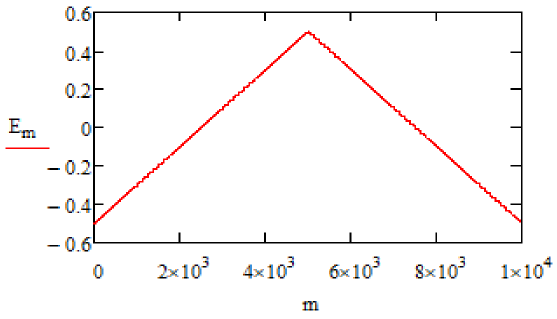
$M := 25$ number of time increments in a single potential step

$d := \frac{\tau}{M}$ time increment (in s)

$2 \cdot \frac{\Delta E}{dE} = 400$ total number of potential steps

$m := 1 .. 2 \cdot \frac{\Delta E}{dE} \cdot 25$ serial number of time increments

$$E_m := \mathrm{if}\left[m \le \frac{\Delta E}{dE} \cdot 25, Es + \left(\mathrm{ceil}\left(\frac{m}{25}\right) \cdot dE - dE\right), Ef - \left[\mathrm{ceil}\left[\frac{m - \left(\frac{\Delta E}{dE} \cdot 25\right)}{25}\right] \cdot dE - dE\right]\right] \qquad \text{potential ramp} \qquad (3)$$



$F := 96485$	Faraday constant
$T := 298.15$	thermodynamic temperature
$R := 8.314$	Gass constant
$n := 1$	stoichiometric number of electrons
$\Phi_m := n \cdot \frac{F}{R \cdot T} \cdot E_m$	dimensionless potential **(4)**
$D := 5 \cdot 10^{-6}$	common diffusion coefficient in cm^2/s
$ks := 0.005$	electrochemical standard rate constant in cm/s
$\alpha := 0.5$	electron transfer coeffcient
$kf := 3$	forward rate constant of the chemical recation in s^{-1}
$kb := 10$	backward rate constant of the chemical reaction in s^{-1}
$Keq := \frac{kf}{kb}$	equilibrium constant of the follow-up chemical reaction
$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}}$	dimensionless electrode kinetic parameter
$Kchem := (kf + kb) \cdot \tau$	dimensionless chemical kinetic parameter

$S_m := \sqrt{m} - \sqrt{m-1}$ numerical integration parameter **(5)**

$M_m := \operatorname{erf}\left(\sqrt{\text{Kchem}\cdot\frac{m}{25}}\right) - \operatorname{erf}\left[\sqrt{\text{Kchem}\cdot\frac{(m-1)}{25}}\right]$ numerical integration parameter **(6)**

$$\Phi_1 := \frac{K\cdot e^{\alpha\cdot\Phi_1}\left(\frac{\text{Keq}}{\text{Keq}+1}\right)}{1 - K\cdot e^{\alpha\cdot\Phi_1}\left[\frac{-2\cdot\text{Keq}}{\sqrt{25\pi}\cdot(1+\text{Keq})} - \frac{M_1}{\sqrt{\text{Kchem}}\cdot(\text{Keq}+1)} - \frac{2\cdot e^{-\Phi_1}}{\sqrt{25\cdot\pi}}\right]} \quad (7)$$

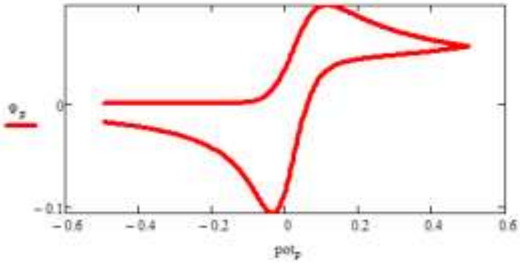
Recurrent formulas for calculating the dimensionless current

$$\Phi_m := \frac{K\cdot e^{\alpha\cdot\Phi_m}\left[\frac{\text{Keq}}{\text{Keq}+1} - \left[\frac{2\cdot\text{Keq}}{\sqrt{25\pi}\cdot(1+\text{Keq})} + \frac{2\cdot e^{-\Phi_m}}{\sqrt{25\cdot\pi}}\right]\sum_{j=1}^{m-1}\left(\Phi_j\cdot S_{m-j+1}\right) - \frac{1}{(1+\text{Keq})\cdot\sqrt{\text{Kchem}}}\cdot\sum_{j=1}^{m-1}\left(\Phi_j\cdot M_{m-j+1}\right)\right]}{1 - K\cdot e^{\alpha\cdot\Phi_m}\left[\frac{-2\cdot\text{Keq}}{\sqrt{25\pi}\cdot(1+\text{Keq})} - \frac{M_1}{\sqrt{\text{Kchem}}\cdot(\text{Keq}+1)} - \frac{2\cdot e^{-\Phi_m}}{\sqrt{25\cdot\pi}}\right]} \quad (8)$$

$p := 1 .. 2\cdot\frac{\Delta E}{dE} - 1$ serial number of potential steps **(9)**

$\Phi_p := \Phi_{\left(\frac{\tau}{d\cdot 25}\cdot p\right)\cdot 25}$ dimensionless current at the end of each potential step **(10)**

$\text{pot}_p := \text{if}\left[p \le \frac{\Delta E}{dE}, \text{Es} + p\cdot dE, \text{Ef} - \left(p - \frac{\Delta E}{dE}\right)\cdot dE\right]$ potential value of each potential step in V **(11)**



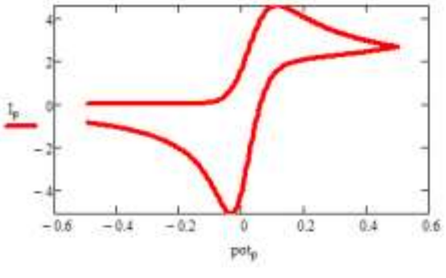
dimensionless cyclic staircase voltammogram

$S := 0.05$ electrode surface area in cm²

$c := 1\cdot 10^{-6}$ bulk concentration of the electractive reactant in mol/cm³

$A := n\cdot F\cdot S\cdot c\cdot\left(\sqrt{\frac{D}{\tau}}\right)$ amperometric constant

$I_p := 10^6\cdot\Phi_p\cdot A$ real current in µA



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