Cyclic Voltammetry (CV) Simulator Written in Microsoft Excel

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Description

The enclosed file is an updated version of a simple cyclic voltammetry (CV) simulator written in Microsoft Excel.[1] The spreadsheet supports up to three chemical species that can undergo up to four redox processes each. The calculations assume that the first process is an electron transfer. Experimental CVs containing up to 10,000 data points in text format can be copied/pasted into the spreadsheet for comparison to the simulation. The spreadsheet can be operated in protected mode or unprotected and modified as needed. The spreadsheet is provided with no guarantee and it may not be suitable for all applications.

System requirements: Microsoft Windows 8.1 Office software or later. New version (v_24) uploaded to the ACS Network on 8/26/21.

Potential values

Enter your formal redox potential ($E^{o\prime}$) values in the order in which they occur in your proposed electrochemical mechanism. Mark the unused formal potentials as N/A (i.e., use the abbreviation for not applicable) to exclude them from the model. Set the starting potential (E_1) value greater than the switching potential (E_2) if reduction occurs during the forward scan. Reverse this order if oxidation occurs during the forward scan.

Optimization macro

The spreadsheet contains a least-squares optimization macro to help simulate experimental data. To run the macro, click on a parameter and then press [Ctrl] o. The macro adjusts the selected parameter and attempts to reduce the root-mean-square (RMS) error of the simulation. The more

calculations a parameter affects, the longer the process takes to complete. Note that the macro could generate a local minimum rather than a true optimization, so visual inspection is necessary to ensure that the simulation has been improved.

Software updates

Revised the code associated with the coupled homogeneous chemical reactions on 8/23/21. Note that entering a homogenous rate constant affects the concentrations of all subsequent subspecies in the electron transfer cycle. This revision simplifies the interpretation of the homogeneous rate constants that are used in the simulation.

Increased the flexibility of the code that removes unused formal redox potentials from the model on 6/2/21. Mark unused formal redox potential ($E^{o\prime}$) values as N/A (i.e., use the abbreviation for not applicable) to exclude them from the model. This update allows for easy conversion between using reduction or oxidation during the forward scan.

Added first- and second-order homogeneous rate constants (k_{A1}, k_{A2}) that add a subspecies back into the electron transfer cycle on 2/24/21.[2–3] This new feature required additional diffusion grids in order to keep track of the removed subspecies. Note that this update roughly doubled the size of the spreadsheet and causes a slight delay in the calculations.

Applied the Feldberg stretching function to the diffusion grids on 2/21/21.[4] Setting the stretching parameter $\gamma = 1$ gives linear diffusion grids with equal spacing between the concentration points. Setting $\gamma > 1$ places several points closer to the simulated electrode surface. Setting $\gamma < 1$ places several points further from the electrode surface. Note that extreme grid stretching will distort your simulations, so adjust this parameter only as needed.

Current convention variable added on 7/28/20. Setting the current convention (*CC*) equal to the letter I (for IUPAC) defines the simulated anodic and cathodic currents as positive and negative respectively. Setting *CC* equal to the letter P (for Polarographic) reverses these definitions. Note that you may need to adjust the graphics in the spreadsheet if you change the current convention.

The resolution of the potential axis was increased from 200 to 600 points to better accommodate wide scan widths on 3/10/20. The total simulation graphic was then brought to the foreground for clarity. This revision tripled the size of the Excel file and caused a slight delay in some of the calculations. The Excel multi-threaded calculation option is now enabled to minimize the delays.

Incorporated separate diffusion coefficients for all subspecies on 9/20/19.[5] Previous versions of this spreadsheet used "common" diffusion coefficients for members of the same redox couple to simplify the calculations. This update provides better control of the diffusion coefficients.

Added a Total simulation graphic to the Import data page to help users optimize the background parameters on 5/31/18. First, copy/paste your experimental data into the Import data page. Then adjust the Offset parameter to zero the baseline of your CV. Next, click on the Species 1 tab to begin your simulation. You can then return to the Import data page at any time to optimize your Gain and Offset parameters based on your simulation.

Incorporated the Saul'yev RL variant to simulate Fick's Second Law of Diffusion on 1/8/17.[4] This method can calculate thinner reaction layers than the combined Taylor series that was used previously. Reducing the variable x_{Scale} reduces the length of the diffusion grids and places the concentration points closer to the working electrode surface. However, using diffusion grids that are too short or long will distort your simulations, so adjust this parameter only as needed.

Separated the equations involving the number of electrons in the rate-determining step from the total number of electrons transferred on 12/22/16.[2] The number of electrons in the rate-determining step (n_a) now controls the peak width. The total number of electrons transferred (n) now controls the total current.

Bug report

Fixed a bug in the diffusion profile graphics for species 6* on 2/15/25. Corrected a typo in the optimization macro addressing on 7/24/21. Bug in the homogeneous reaction calculations was fixed on 1/14/21. Corrected a typo in the standard heterogeneous rate constant for the second

redox couple on 11/2/20. Bug in the calculations for the data selection process was corrected on 1/14/20. Bug in the diffusion profile graphics for species 4 was corrected on 6/26/19. Bug in the Import data graphics was corrected on 12/31/15.

References cited

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3. Gosser, Jr. D. in *Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms*, VCH Publishers: New York, **1993**, ISBN: 1-56081-026-2.

4. Britz, D. in *Digital Simulation in Electrochemistry 3^{ed} ed.*, Springer: Berlin, **2010**, ISBN: 978-3-642-06307-7.

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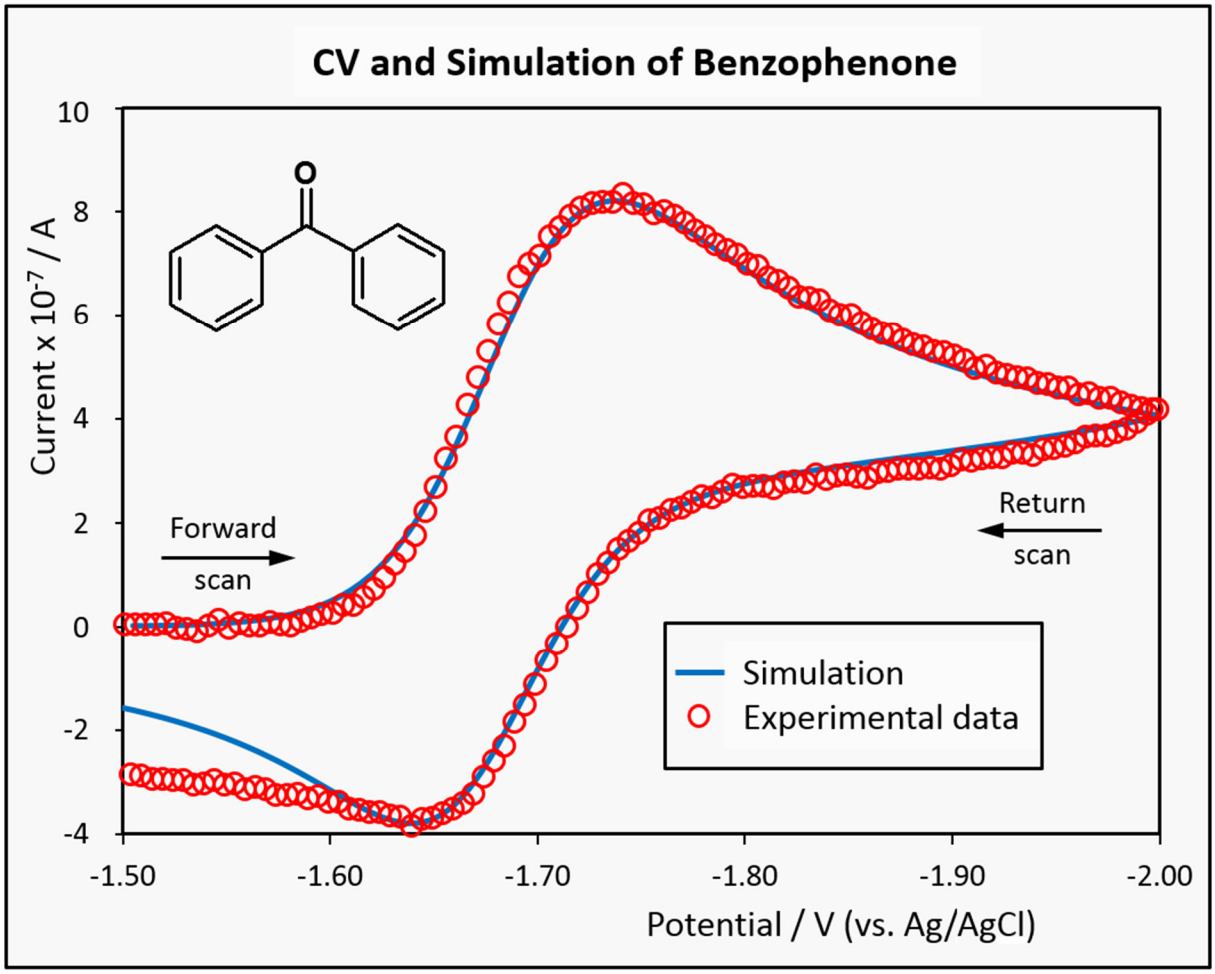
Appendix I. Spreadsheet parameters

Several parameters from the first version of this spreadsheet were renamed to incorporate new features. The table below describes the parameters that are used in the newest version of the spreadsheet. Symbols in the spreadsheet written as subscripts in parentheses after a parameter indicate the associated subspecies.

Parameter	Definition	Value and/or unit(s)
A	Surface area of the working electrode.	cm^2
α	Transfer coefficient for a redox couple.	≈ 0.5 (unitless)
C_{Bulk}	Concentration of the bulk solution.	mol/cm^3
CC	Current convention that will be used for the simulated current.	Letter I or P
D	Diffusion coefficient for a subspecies.	≈ 1 x 10^{-5} cm^2/s
E_1	Starting potential of the CV experiment.	V
E_2	Switching potential of the CV experiment.	V
$E^{o\prime}$	Formal potential for a redox couple.	V or N/A
γ	Stretching parameter. γ= 1 gives linear diffusion grids. $\gamma >$ 1 moves several concentration points closer to the electrode surface. $\gamma <$ 1 moves several concentration points further from the electrode surface.	≈ 1 (unitless)
Gain	Amplification factor for the experimental background.	Unitless multiplier
k^o	Standard heterogeneous rate constant for an electron transfer.	cm/s
k_{R1}, k_{R2}	First- and second-order homogeneous rate constants respectively for reactions that remove a subspecies from the electron transfer cycle.[a]	s^{-1}, $cm^3/mol•s$ respectively
k_{A1}, k_{A2}	First- and second-order homogeneous rate constants respectively for reactions that add a subspecies back into the electron transfer cycle.	s^{-1}, $cm^3/mol•s$ respectively
n	Total number of electrons transferred per subspecies (controls total peak area).	Unitless
n_a	Number of electrons transferred in rate determining step (controls peak width).	Unitless (often 1 or 2)
Offset	Constant added to experimental current.	A
T	Sample temperature during experiment.	K
v	Scan rate used during the experiment.	V/s
x_{Scale}	Compress or expand x-axes of diffusion grids.	Percentage (%)

a) You can couple a first- or second-order homogeneous reaction to each electron transfer, but you cannot couple both accurately at the same time.[4]

Appendix II. Figure of cyclic voltammetry (CV) data and simulation for benzophenone