

DigiElch 5™ from ElchSoft is a simulation program for electrochemical experiments. DigiElch 5 offers a number of unique features:

- Fitting multiple data files to a mechanism to extract kinetic and thermodynamic properties.
- Exact 2-D simulation of band and disk microelectrodes.
- ChronoAmperometry, Square Wave Voltammetry, Impedance Spectroscopy in addition to Cyclic Voltammetry
- Simulation of amalgam formation with mercury electrodes
- Modeling surface adsorption.
- An optional adaptive grid algorithm.
- Improved computational efficiency via parallel processing.

DigiElch 5 simulates user-defined mechanisms consisting of an arbitrary number of charge transfer steps and (first- or second-order) chemical reactions. An extended Frumkin isotherm models adsorption of reactants, products or intermediate chemical species in simple charge transfer processes. All simulations account for effects such as IR-drop and/or double layer charging. Simulations and fitting take advantage of multi-core processors with full control during setup.

The end result of any simulation is a plot of current vs. voltage or time or a plot of impedance vs. frequency. Concentration distance and surface concentration potential curves (as well as surface coverage potential curves) are also available.

DigiElch comes in two varieties:

DigiElch-Standard: Experimental data can be imported and compared with a simulation

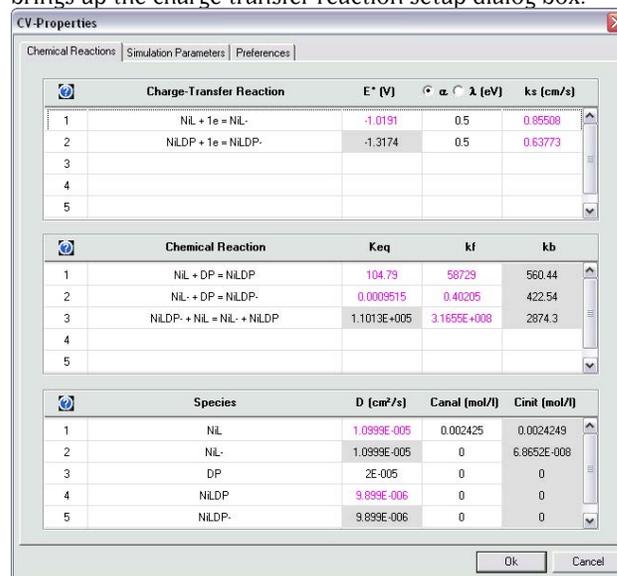
DigiElch-Professional: Multiple experiments employing different analytical concentrations and experimental parameters (e.g sweep rate, switching potential) can be imported and fit to the same model to get reliable kinetic and thermodynamic properties.

Chemistry & Electrochemistry Setup

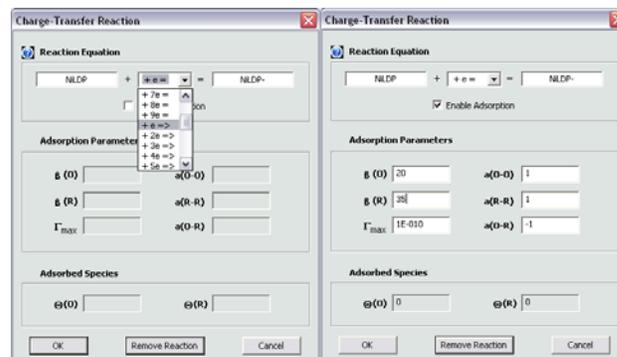
DigiElch 5 can handle an arbitrary number of reactions and species. The electrochemical system is defined by the charge transfer reactions, the coupled chemical reactions and the initial concentrations of the species in solution.

Kinetics of the system can obey either Butler-Volmer (BV) or Marcus equations. The BV equation requires a transfer coefficient (α) and Marcus equation requires the reorganization energy (λ). BV kinetics can be setup for single or multi-electron transfer. Left-clicking on any of the charge transfer reactions on the parent setup screen

brings up the charge transfer reaction setup dialog box.



Typical Parent Setup Screen of an ECE System. The chemistry and the electrochemistry of the system can be defined through the parent setup screen.



Reaction Setup Dialog Box The reactions can be fully reversible or irreversible with multiple electrons (shown on the left). Adsorption of either chemical species can also be incorporated through an expanded Frumkin isotherm by defining " β " and " a " values (as shown on the right)

The rate constants will be calculated based on the selections and the parameters entered in the parent dialog box. k_f or k_b can be forced to be zero by choosing irreversible reactions.

Adsorption of any species involved in the electrochemical reactions can be incorporated into the simulation via an expanded Frumkin isotherm. This formulation includes interactions between the oxidized and the reduced species in addition to interactions between species of the same sort. The parameters available for oxidized species (O) and

reduced species (R) are the strength of adsorption β and maximum coverage Γ_{\max} . The interaction parameter \mathbf{a} is available for self interactions (i.e., O-O and R-R) and cross interactions (i.e., O-R).

Chemical Reaction	Keq	kf	kb
1 NL + DP = NLDP	50	10000	200
2 NL + DP = NLDP	0.001	1	1000
3 NLDP + NL = NL + NLDP	50000	1E+009	20000
4			
5			

Chemical Reaction

NLDP + NL = NL + NLDP

OK Help Remove Cancel

Chemical Reaction Setup Dialog Box The chemical reactions can be setup as unimolecular or bimolecular reactions using any chemical species of choice.

Left clicking any of the chemical reactions will bring up the chemical reaction setup dialog box shown above. The thermodynamic and the kinetic parameters of a given chemical reaction (i.e., K_{eq} , k_f , k_b) need to be entered in the parent setup screen as shown above. Due to the mathematical dependence of the variables, K_{eq} and k_f can be individually manipulated and k_b is calculated from those two.

Species	D (cm ² /s)	Conal (mol/l)	Cinit (mol/l)
1 NL	1.0999E-005	0.002425	0.0024249
2 NL-	1.0999E-005	0	6.8652E-008
3 DP	2E-005	0	0
4 NLDP	9.899E-006	0	0
5 NLDP-	9.899E-006	0	0

Bottom Part of the Parent Setup Screen The diffusion coefficients and the analytical concentrations of the chemical species can be adjusted. The initial concentrations are calculated depending on the pre-equilibria preference discussed later.

Experiment Setup

In the setup window, the experimental waveform can be specified (details will follow in the relevant sections). The rest of the parameters in this window are common to all experiments. They control experimental and computational details. The pre-equilibrium option establishes the initial concentrations at the starting potential (which may or may not be different from the analytical concentrations). The three available options are:

Disabled: No calculations are performed. The analytical concentrations are used as initial concentrations. Ideal for experiments where solution is prepared and the experiment is started at the initial potential without any time for the solution and the electrodes to equilibrate.

Enabled: The initial concentrations are calculated using the Nernst Equation for the electrochemical reactions and the equilibrium equation for chemical reactions. Ideal for

experiments where the solution is given enough time to fully come to equilibrium at the initial potential.

Smart: Nernst Equation is not used but the analytical concentrations are reassigned depending on the initial potential and the standard potentials. The initial concentrations are then calculated using the chemical equilibria with the analytical concentrations. This is a more realistic calculation since there is not enough time for a full equilibrium to establish in real experiments.

The geometry of the electrode can be varied from planar to spherical for 1-D simulations and between band and disk for 2-D simulations. For a spherical mercury electrode, the amalgam formation process can also be modeled for any of the species involved in the simulation.

CV-Properties

Chemical Reactions | Simulation Parameters | Preferences

Scan use same v [V/s] in all scan segments

Segment	Estart [V]	Eend [V]	v [V/s]
1	-0.75	-1.55	200
2	-1.55	-0.75	200
3			
4			

Potential steps [V] 0.001

Pre-Equilibrium Disabled Enabled Smart

Geometry Spherical (Hg) Spherical (Pb) Spherical (Hg) Hemispherical Cylindrical Hemicylindrical

Diffusion Semi-Infinite 1D

Species Amalgam NL ND NL- ND DP ND

Model Parameters Noise level (%) 0 Gauss-Newton iterations 2 Exp. factor for x-grid 0.5 Rel. truncation error (%) 0.0001 Xmax/SQRT(Dt) 6

2D-Simulation Exp. factor for y-grid Boxes for electrode

FEM-Simulation Local FEM error 0.005

Experimental Conditions Ru (Ohm) 0 Cdl (F) 0 Temp. (K) 298.2

Simulation Name D:\Test\NLDP1\CV200M13.use

Ok Cancel

Setup Screen for the Simulation Parameters Electrode geometry, dimensionality, pre-equilibria, and a range of computational parameters

A thin layer cell is simulated by changing the diffusion option to finite 1-D and specifying the length of the cell. The boundary condition at the far end of the cell can be individually specified to be either ORB (Open Right Boundary) or BRB (Blocked Right Boundary). ORB fixes the concentration gradient to be zero and BRB fixes concentration to be C_{init} at the far end of the cell.

There are a number of computationally critical parameters that determine the balance between performance and accuracy of the simulations. The default parameters are chosen for accurate simulations that are reasonably fast. Detailed information on these parameters can be found under the help menu of the program.

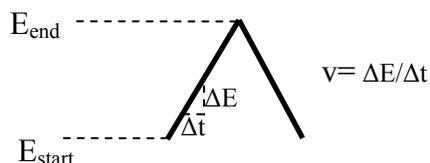
Additionally, the effects of uncompensated resistance and double layer capacitance can be investigated. Both these effects can be a real nuisance in a number of experiments and even dominate the response in faster experiments. Using DigiElch 5 the effect can be predicted and compared with the expected result of any electrochemical system. The effects of temperature can also be easily investigated.

Cyclic Voltammetry (CV) Simulations

Cyclic Voltammetry (CV) is commonly the first experiment performed in any physical electrochemical study. Potential is swept over a wide range in search of redox couples. Once found, the redox couple is investigated with varying sweep rates, scan limits, and analytical concentrations.

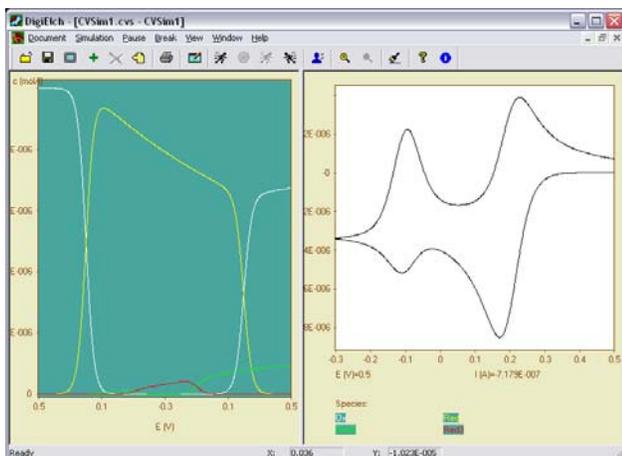
Segment	Estart (V)	Eend (V)	v (V/s)
1	-0.7	-1.4	10
2	-1.4	-0.7	10
3			
4			

Potential steps (V) 0.001



CV setup and anatomy of the CV signal Three parameters define the signal. E_{start} , E_{end} , and sweep rate are available on the setup screen as shown.

The simulation parameters for CV include an independently adjustable sweep rate for every segment of the sweep, the scan limits of each segment, and the size of the potential steps between data points. Copying the E_{start} value for a segment from the E_{end} value from the previous segment keeps the entire experiment continuous.

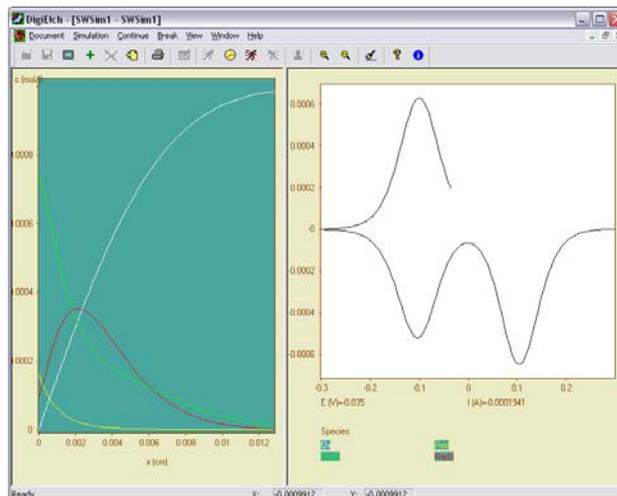


CV and concentration potential profiles The simulations can include adsorbed species as well as species diffusing from solution.

Square Wave Voltammetry (SWV) Simulations

Square Wave Voltammetry (SWV) is routinely employed to suppress the background current in cyclic voltammetry. Its ability to discriminate against slow events in favor of fast ones can be used to separate multiple redox events occurring at the same potential.

DigiElch 5 can simulate SWV experiments in any of the systems explained before; there is no restriction on the geometry or the chemistry.

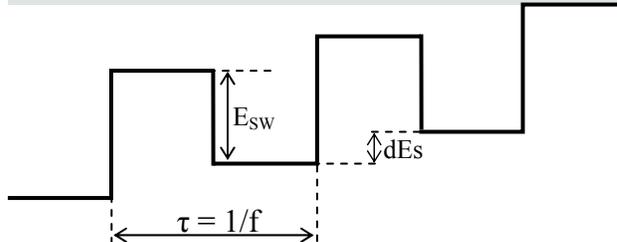


SWV simulation and concentration profiles Square waves and concentration profiles can also be simulated with any of the systems described in the CV section.

A square wave signal as shown in the figure below is applied and the current measurements are taken at the middle ($\tau/2$) and the end of every period (τ). This way the capacitive background currents decay and a more direct measurement of the faradaic current is possible.

Segment	Estart (V)	Eend (V)	f (Hz)
1	0.3	-0.3	100
2	-0.3	0.3	100
3			
4			

dEs (V) 0.005
Esw (V) 0.025
Time steps/half-cycle 15



SWV scan setup and anatomy of the SWV signal Three parameters define the signal. f , dE_s and E_{sw} are available on the setup screen.

The setup of the square wave is also divided into segments much like the CV experiments. A separate frequency f and potential limits can be specified for each segment.

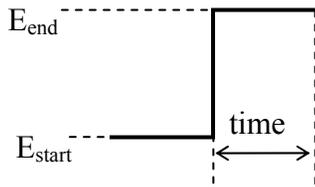
ChronoAmperometry (CA) Simulations

ChronoAmperometry (CA) involves holding the potential constant for a period of time while the current is measured. At the end of the time period the potential is stepped to a new value and the current measurement continues. The waveform and the setup parameters are shown in the figure below.

Scan use same time [s] in all scan segments

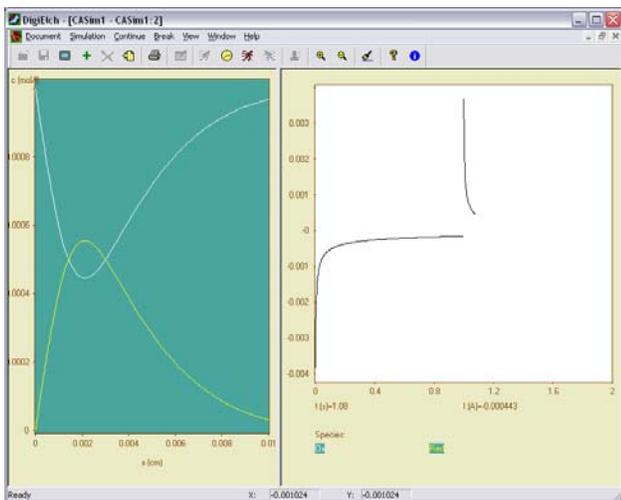
Segment	Estart (V)	Eend (V)	time (s)
1	0.3	-0.3	1
2	-0.3	0.3	1
3			
4			

Time steps/segment 500



CA setup and anatomy of the CA signal Three parameters define the signal. E_{start} , E_{end} and time are available on the setup screen as shown.

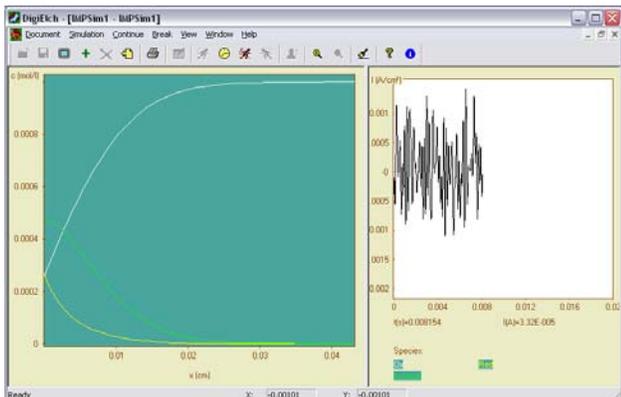
In the CA setup screen, the potentials and the time intervals of the segments can be independently specified.



CA simulation and concentration profiles ChronoAmperometry and concentration profiles can also be simulated with any of the systems described in the CV section

Multi-Sine Impedance (IMP) Simulations

Electrochemical Impedance Spectroscopy can be simulated using a multiple sine excitation. A multi-sine voltage signal is applied to the system and the resulting current is simulated as shown in the figure. The impedance spectrum is then calculated by a Fourier transform of the time signal.



IMP simulation The IMP signal is applied in time domain where the concentration profiles can be plotted in an evolving fashion.

During the simulation, concentration distance and concentration time plots are also available as shown below. The calculated impedance can be fully or partially corrected for IR effects.

The AC simulation starts with a constant potential preconditioning step. The initial concentrations are calculated to be in equilibrium at E_{start} and then the potential is stepped to E_{dc} and for the specified length.

At the end of the DC experiment, the AC-Signal is applied. The definition of the AC signal involves the fundamental amplitude (dE_{ac}), the number of AC-Packets, the number of applied frequencies (up to 15), and the fundamental frequency (f_{min}). The maximum frequency is calculated using the signal definition and cannot be modified. The signal applied will be composed of AC-Packets that are f_{min}^{-1} in length.

DC-Signal	AC-Signal
Estart (V) 0.3	Define Signal Applied Frequencies 15
E _{dc} (V) 0	dE _{ac} (V) 0.015 f _{min} (Hz) 100
DC-Time (s) 5	AC-Packets 10 f _{max} (Hz) 5050

IMP setup The simulated IMP experiment can be setup with a DC conditioning step before the AC experiment. E_{start} , E_{dc} and DC-Time relate to the conditioning step, while details of the IMP experiment are given in the AC-Signal box.

Define Signal

Amplitude Settings

- Set relative amplitude equal to 1 for each frequency
- Set relative amplitude equal to 1/sqrt(f)
- Set relative amplitude individually for each frequency

Index, i	f(i)/f ₀	Phi(i)	A(i)/A ₀
1	2	3.676	1
2	3	2.201	1
3	5	5.17	1
4	7	1.094	1
5	11	4.464	1
6	17	1.91	1
7	23	0.574	1
8	29	0.926	1
9	37	6.211	1
10	47	0.748	1
11	59	0.056	1
12	67	3.341	1
13	79	3.781	1
14	89	1.045	1
15	101	2.832	1

f = frequency, Phi = phase angle, A = Amplitude

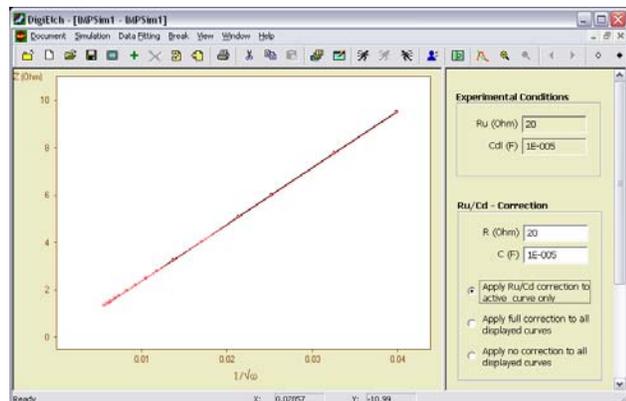
OK Reset Default Signal Cancel

IMP signal definition The signal can be defined with up to 15 frequencies with individual frequencies phases and amplitudes. The amplitudes can be fixed to the fundamental amplitude, defined to be $1/\sqrt{f}$ or adjusted individually.

Individual AC-Packets can be defined by assigning phase and amplitude to each component using the "Define Signal" button. When defining the signal, the frequency and the amplitudes are assigned relative to the corresponding fundamental parameter in the parent dialog box. The

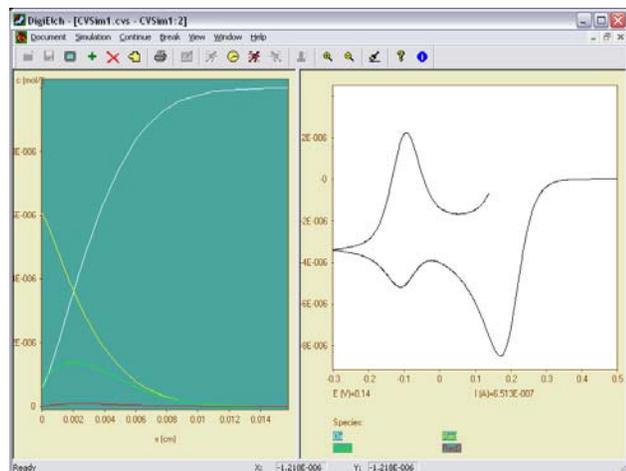
signal generated in this way is then adjusted in such a way that the maximum value of the amplitude becomes equal to the value entered for dE_{ac} .

The real and imaginary impedances (Z_r and Z_i) can be displayed in three ways: Z_i and Z_r vs $1/\sqrt{\omega}$, $\cot(\phi)$ vs. $\sqrt{\omega}$, and Z_i vs. Z_r , where $\cot(\phi)$ is the cotangent of the phase angle (i.e., Z_r/Z_i) and ω is the angular frequency (i.e., $2\pi f$).



IMP simulation and IR correction Impedance spectroscopy can be simulated with any of the systems.

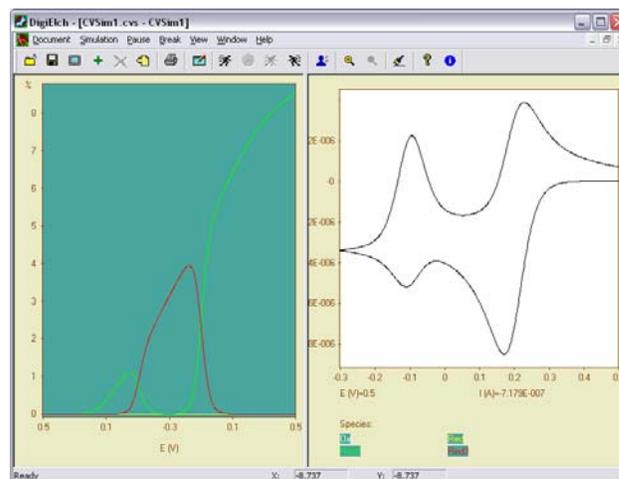
Concentration and Coverage Profiles



The concentration distance curve An evolving concentration distance curve will be shown concurrent with the CV.

Concentration gradients and surface coverages are the centerpiece of any electrochemical experiment. For species diffusing to the electrode, the current is given by Fick's first law of diffusion. A side by side view of concentration profiles with the CV curve aids the interpretation of complex systems and provides a useful teaching tool for simple systems.

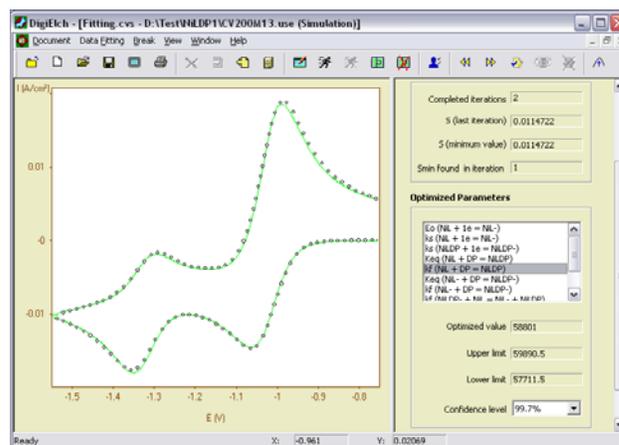
DigiElch 5 can display concentrations as a function of potential or distance and coverages of the adsorbed species as a function of potential. The concentration-distance plots can be drawn concurrent with the simulation performed. This way the simulated concentration profiles can be shown at any given instance of the experiment.



The coverage potential curve The coverage of the surface adsorbed species can be displayed as a function of potential as percent coverage of the Γ_{max} entered during setup.

Experimental Data Fitting (DigiElch-Professional Only)

DigiElch 5 comes in two varieties: DigiElch Standard and DigiElch Professional. Experimental data can be imported into either version of DigiElch and compared with the simulated data. Using DigiElch Professional a non-linear least squares fitting algorithm can be simultaneously applied to multiple experimental curves simultaneously. One can use multiple data files taken with different analytical concentrations and experimental parameters (e.g. scan rate and scan limits for cyclic voltammetry) that all fit to the same mechanism.



CV fitting A group of data files, imported into DigiElch can be fit to a mechanism.

The parameters to be fit can be chosen to be any or all of:

- redox potentials (E^0)
- rate constants (k_s)
- transfer coefficients (α)
- equilibrium constants (K_{eq})
- rate constants (k_f)
- diffusion coefficients (D)

Diffusion coefficients of two or more species can be kept identical throughout the fitting procedure.

Parallel Processing Support

Modern computers employ multi-core processors for more efficient computation. DigiElch 5 employs parallel processing at five separate user controlled levels. This allows the user immense control over the resources of the computer and the time it takes to run the fitting routines. At the maximum parallelization level, the computation time can decrease by factors of two and four for dual core and quad core CPUs respectively.

System Information

DigiElch 5 requires 32- or 64-bit version of Windows XP or Windows Vista. The efficiency of the simulations and fitting strongly depend on the specifics of the computer. DigiElch is compatible with data taken using Gamry Instruments PHE200 and PV220 systems. It may also be compatible with other data formats. Contact Gamry Instruments regarding other data formats.



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