

## Lesson 0:

This lesson demonstrates most of the basic features of *DigiElch* such as running a simulation, copying & pasting simulation objects, saving and exporting of simulation data, customizing colors and screen display, zooming the screen display, retrieving the coordinates of individual current points etc. For this purpose we are going to simulate a cyclic voltammogram (CV) for a simple charge-transfer mechanism that refers to a CV-experiment measured in the potential range between 0 and -1V at a mercury drop electrode with a scan rate of 10 V/s. The size of the mercury drop corresponds to a mercury mass of 4 mg. In the next step it is investigated how the shape of the current curve changes if first- and second-order chemical reactions are coupled with the charge-transfer process in the form of follow-up reactions.

When working through the lesson, please, keep in mind that some menu commands may be disabled as long as *DigiElch* is running as trial installation.

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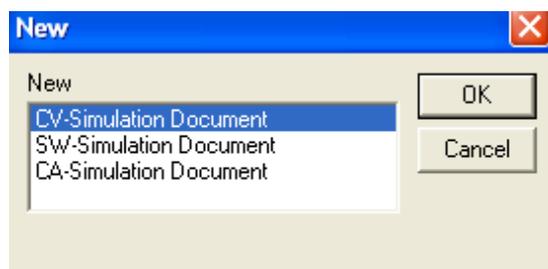
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# 1. Running a cyclic voltammetric simulation

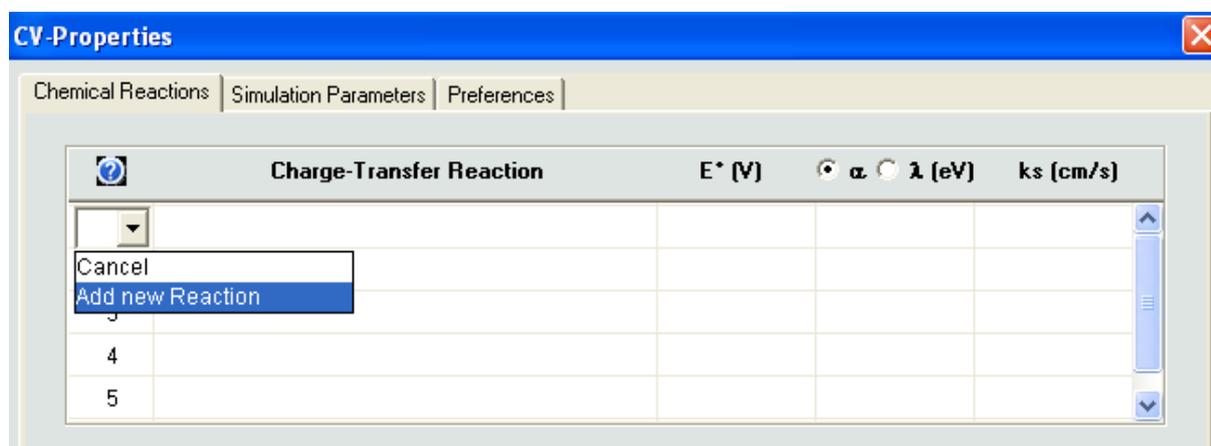
## 1.1. Starting the program and selecting the document type for running cyclic voltammetric simulations



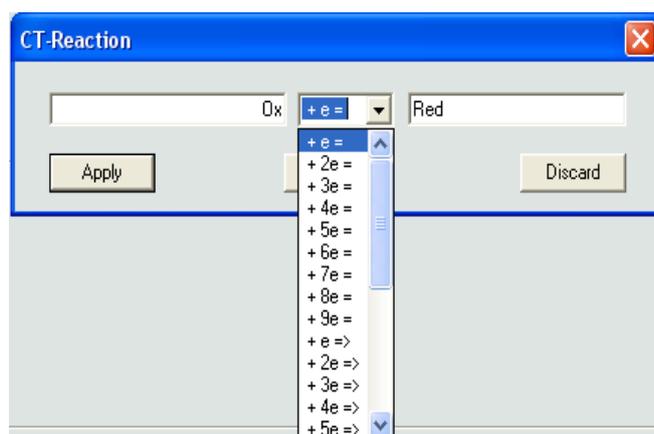
Start *DigiElch*, click on **File -> New** (  ) and select **CV-Simulation Document** in the appearing dialog-box

## 1.2. Defining a simple charge transfer mechanism

Click on **Simulation -> Edit Properties** (  ) and make sure that the **Chemical Reactions** page is activated. For entering the charge-transfer reaction, click on the left-most index field associated with the first empty line in **Charge-Transfer Reaction**. The index field will be transformed into a combo box offering the options shown in following picture



Select **Add new Reaction** and complete the appearing charge-transfer reaction template



### Meaning:

Ox: Name of the species representing the oxidized form

Red: Name of the species representing the reduced form

### Reaction Types:

**$Ox + e^- = Red$**

( $k_f$  and  $k_b$  computed from Butler-Volmer or Marcus equation)

**$Ox + ne^- = Red$  ( $n=2, 3, 4, \dots, 9$ )**

( $k_f$  and  $k_b$  computed from Butler-Volmer equation)

**$Ox + e^- \Rightarrow Red$**

( $k_f$  computed from Butler-Volmer or Marcus equation,  $k_b = 0$ )

**$Ox + ne^- \Rightarrow Red$  ( $n=2, 3, 4, \dots, 9$ )**

( $k_f$  computed from Butler-Volmer equation,  $k_b = 0$ )

( $k_f$  and  $k_b$  computed from Butler-Volmer equation)

**$Ox + e^- \Leftarrow Red$**

( $k_b$  computed from Butler-Volmer or Marcus equation,  $k_f = 0$ )

**$Ox + ne^- \Leftarrow Red$  ( $n=2, 3, 4, \dots, 9$ )**

( $k_b$  computed from Butler-Volmer equation,  $k_f = 0$ )

## Remarks

- Whether the Butler-Volmer – or Marcus- equation is used for computing  $k_f$  and  $k_b$  depends on whether the  $\alpha$  –button or the  $\lambda$  (eV)- button is activated in **Charge-Transfer Reaction**:



The selection applies to all charge-transfer reactions. It cannot be adjusted individually for each reaction.

- Marcus-kinetics is allowed only for charge-transfer reactions with  $n=1$ . All charge-transfer reactions are reset to Butler-Volmer – kinetics when adding a reaction with  $n>1$ .
- Charge transfer reactions must always be formulated to proceed as a reduction from the left to the right. Whether a charge transfer step does really proceed as reduction or oxidation is determined by the relation between initial and standard potential and the direction of the potential scan.
- The species name of oxidized and reduced form must not be equal or empty.
- Any character (including space) can be used in a species name but the **first** character must not be **X, Y or Z**.

For the purposes of the actual example it is most convenient to stay with the default species names and to select a single (quasi-reversible) charge-transfer step (“+ e =”) in combination with Butler-Volmer kinetics so that  $E^\circ$ ,  $\alpha$  and  $k_s$  have the usual meaning of *standard potential*, *charge-transfer coefficient* and *heterogeneous standard rate constant*. Close the charge-transfer reaction template with **OK** and enter the following values for  $E^\circ$ ,  $\alpha$  and  $k_s$

	Charge-Transfer Reaction	$E^\circ$ [V]	<input checked="" type="radio"/> $\alpha$ <input type="radio"/> $\lambda$ [eV]	$k_s$ [cm/s]
1	Ox + e = Red	-0.5	0.5	1
2				

Complete the **Chemical Reactions** page by entering analytical concentrations for all involved species as shown in the following picture

	Species	D [cm <sup>2</sup> /s]	Canal [mol/l]	Cinit [mol/l]
1	Ox	1E-005	0.001	0
2	Red	1E-005	0	0
3				

### 1.3. Defining the simulation parameters

Activate the **Simulation Parameters** page. Modify the potential scan, select the electrode geometry *spherical* (Hg) and enter a mercury mass of 4 mg as shown in the following pictures

**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	-1	10
2	-1	0	10
3			
4			

Potential steps [V] 0.005

**Geometry**

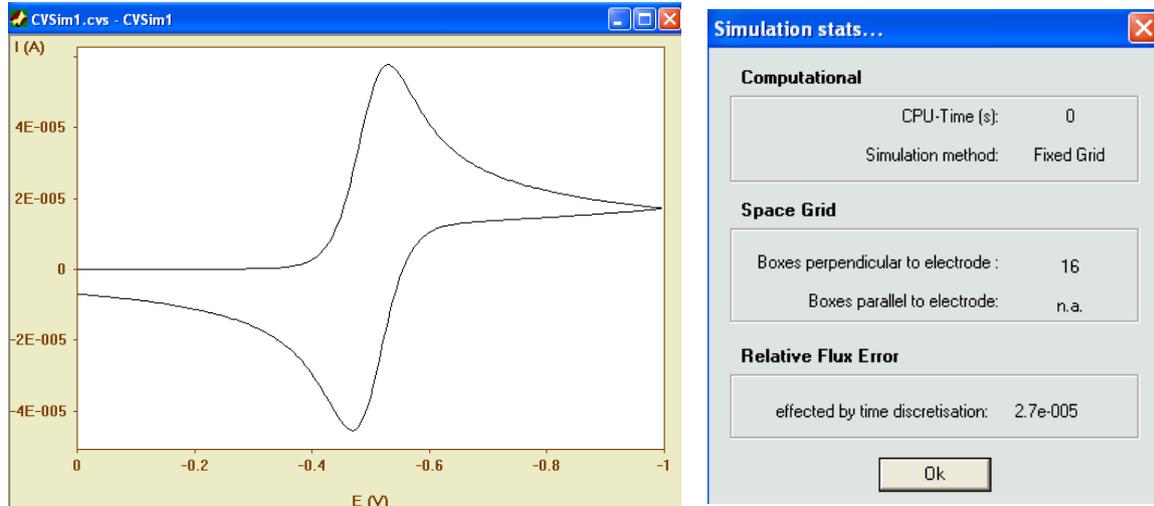
Spherical (Hg)

Mass [mg] 4

Do not modify the remaining parameters close the **CV-Properties** dialog by clicking on **OK**.

#### 1.4. Running the simulation using the Fixed Grid Simulator

Click on **Simulation -> Run -> Fixed Grid Simulation** (). The picture on the left-hand side shows the current curve that should appear as soon as the simulation has terminated

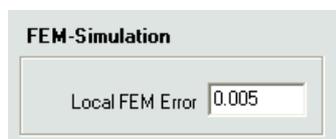


The picture on the right-hand side shows a summary of the simulation stats obtained when clicking on the **Simulation -> Stats** command:

- *CPU-Time(s)*: depends on the CPU-power of the computer; 0 is retrieved if the simulation takes less than one millisecond.
- *Simulation method*: indicates whether the Fixed Grid Simulator or the Adaptive Grid Simulator was used for simulating the CV
- *Boxes perpendicular to electrode*: in the actual case 16 boxes (grid points) were used for simulating the concentration profile in x-direction (perpendicular to the electrode surface)
- *Boxes parallel to electrode*: a value is shown only for a two-dimensional simulation where the number represents the boxes (grid points) used for simulating the concentration profile in y-direction (parallel to the electrode surface)
- *Relative Flux Error effected by time discretisation*: a number is shown only for simulations executed with the Fixed Grid Simulator (box method). For this method it is relatively easy and straightforward to compute an accurate estimate for the relative flux error (resulting from the finite size of the potential steps) at run time.

#### 1.5. Running the simulation using the Adaptive Grid Simulator

Alternatively the simulation can be executed with an Adaptive Grid Simulator based on the *finite element method* (FEM). In this case the simulation starts with the same number and distribution of grid points as used by the Fixed Grid Simulator but additional grid points may be introduced after each time/potential step in order to ensure that the error level in the simulated concentration profiles remains smaller than a predefined value. This **Local FEM Error**-value can be defined on the **Simulation Parameters** page:

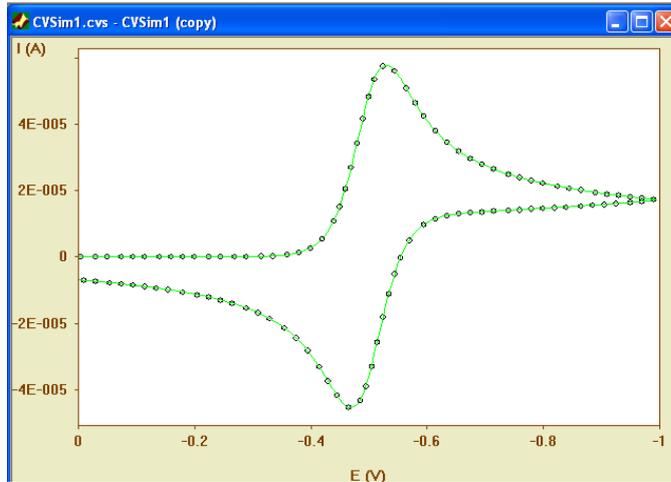


The smaller this value, the more grid points will be used for simulating the concentration profile, the more accurate is the simulated flux, and the longer takes the computation. However, the grid refinement is switched off if *Local FEM Error* = 0. In that case the simulation is executed using the FEM simulator on a fixed expanding grid identical with that used by the box method (“Fixed Grid Simulator”).

Note that the FEM-simulator is second-order accurate for simulating both flux and concentration profiles while the box method is the only method that attains exponential convergence for the simulated flux error. For this reason a significantly higher number of grid points (and significantly higher computational costs) are required by the Adaptive Grid Simulator to achieve a flux-accuracy comparable to that obtained with the box method even when using the latter method on strongly expanding grids. Because of the higher efficiency, the use of the Fixed Grid Simulator is recommended by default.

For demonstrating the higher efficiency of the Fixed Grid Simulator we are going to compare the current curve obtained in 1.4. with that simulated with the Adaptive Grid Simulator. For this purpose we Copy & Paste the fixed-grid-simulation by clicking on **Simulation -> Copy** () and **Simulation -> Paste** (). Note that two

(identical) current curves are shown now on the screen. The **active curve** (referring to the active simulation) is drawn in black by default while the **inactive curve** (referring to the inactive simulation) is drawn in green by default. (The default colors can be changed as described in 4.2). In order to clarify that really two curves are plotted on the screen it may be useful to emphasize the active curve by plotting it in the form of open circles as shown in the following picture



The active curve (drawn in black) is the one to which the commands in the **Simulation-Menu** and in the menu **Active Simulation** of the **View-Menu** refer.

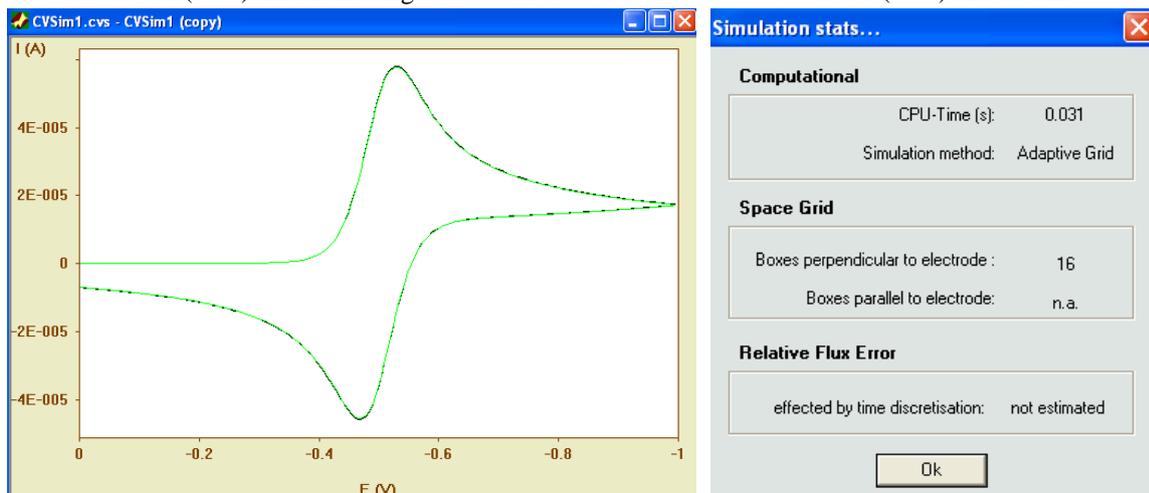
Consequently, clicking on

**View -> Active Simulation -> Use Circles** ()

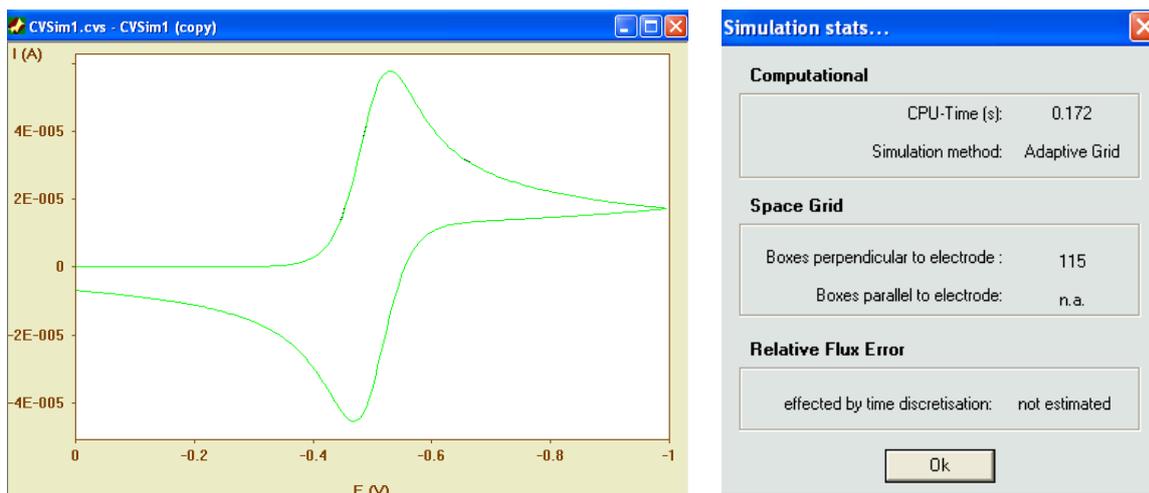
makes that the *active* curve is plotted in the form of open circles while filled circles are used when clicking on

**View -> Active Simulation -> Use Filled Circles** ()

Click on **Simulation -> Edit Properties** () , go to the **Simulation Parameters** page and enter "0" for *Local FEM Error*. Close the **CV-Properties** dialog by clicking on **OK** and click on **Simulation -> Run -> Adaptive Grid Simulation** (). After undoing **View -> Active Simulation -> Use Circles** () one obtains



Since *Local FEM Error* was zero, the FEM-Simulator worked on the same (fixed) 16-points grid as the box method in 1.4. Obviously, the active (black) curve referring to the FEM-simulator is not in perfect agreement with the inactive (green) curve referring to the box method. (The difference in the peak current amounts to about 0.5%). In order to get virtually identical curves it is necessary to repeat the Adaptive Grid Simulation using a *Local FEM Error* of about 0.005 as shown in the following picture

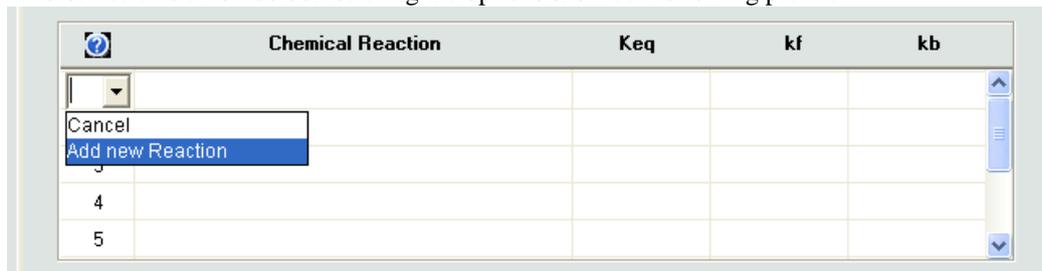


Because of *Local FEM Error* > 0 the adaptive grid refinement was enabled now. About 100 additional grid points have been introduced in the course of the simulation and the current curve converges exactly to that obtained with the box method on the 16-points grid.

### 1.6. Adding a chemical reaction

Now we are going to modify the simple charge-transfer mechanism assuming the reduced species *Red* would undergo a first-order decomposition reaction  $Red \rightarrow P$  (EC-mechanism)

Click on **Simulation -> Edit Properties** (  ) and make sure that the **Chemical Reactions** page is activated. Click on the left-most index field associated with the first empty line in **Chemical Reaction**. The index field will be transformed into a combo box offering the options shown in following picture



Select **Add new Reaction** and complete the appearing chemical reaction template in the following way



**Syntax:** Species1 + Species2 = Species3 + Species 4

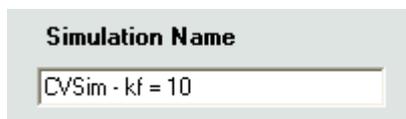
Remarks:

- If the name of a species starts with **X**, **Y** or **Z** it is considered a buffer/excess component. The concentration of such a species does not change in the course of the simulation.
- Excess components or empty strings can be entered only for Species 2 and/or Species 4.
- (Pseudo-) First-Order reaction: Species 2 **and** Species 4 are empty strings (or excess components)
- Second-Order reaction: no species name or only the name of Species 2 **or** 4 is empty or that of an excess component

Close the chemical reaction template with **OK** and enter the following values for the *equilibrium constant*,  $K_{eq}$ , and the (*forward*) *rate constant*,  $k_f$

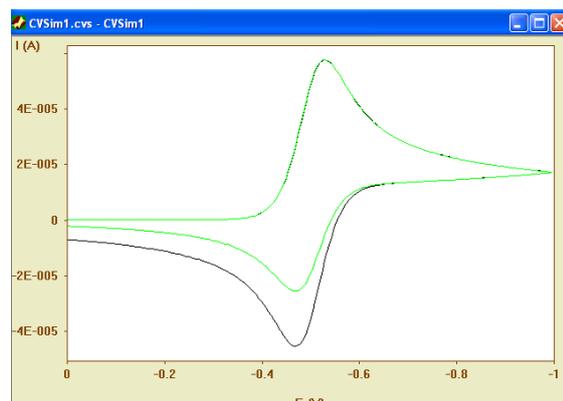
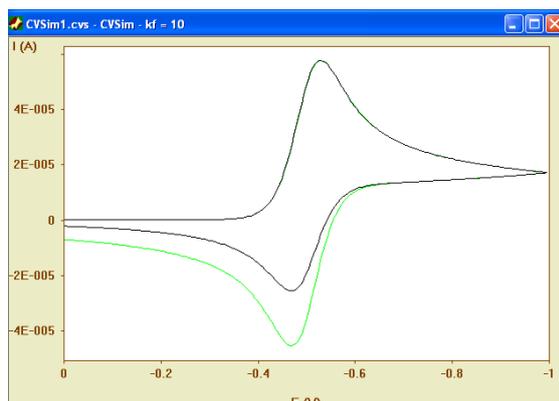
	Chemical Reaction	Keq	kf	kb
1	Red = P	10000	10	0.001
2				

A large value of  $K_{eq}$  ( $\geq 10000$ ) was used in order to make the reaction “irreversible”.



Go to the **Simulation Parameters** page and enter “CVSim – kf = 10” as simulation name to make it easier to distinguish this simulation from the first one referring to the simple charge transfer mechanism.

Close the **CV-Properties** dialog by clicking on **OK** and run the simulation as described in **1.4**. The screen display should look now as shown in the picture on the left-hand side where “CVSim – kf = 10” is the active simulation.



That means, the parameters shown when clicking on **Simulation -> Edit Properties** (  ) refer to the EC-mechanism. Click on **View -> Activate Next Simulation** (  ) to activate the simulation referring to the simple charge-transfer mechanism as shown above in the picture of the right hand side.

Now we are going to investigate what happens if the (*forward*) *rate constant*,  $k_f$ , becomes larger and larger. For this purpose make sure that “CVSim –  $k_f = 10$ ” is the active simulation, Copy & Paste this simulation and open the the **CV-Properties** dialog again. (For convenience, these three commands are executed when clicking on

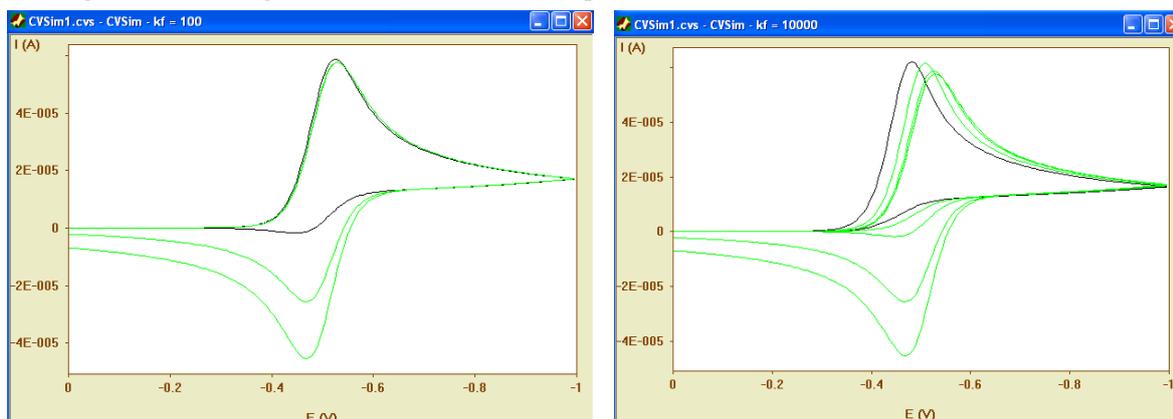
**Simulation -> Duplicate** (  ). Make the following modifications on the **Chemical Reactions** and **Simulation Parameters** page, respectively:

Chemical Reaction	Keq	$k_f$	$k_b$
1 Red = P	10000	100	0.001
2			

**Simulation Name**

CVSim -  $k_f = 100$

Running the simulation gives the results shown in the picture on the left-hand side.



Repeating the same steps for  $k_f = 1000$  and  $k_f = 10000$  results in the picture shown on the right-hand side.

### 1.7. Editing (modifying) or removing a reaction equation

Now we are going to investigate under which conditions a second-order follow up reaction becomes (pseudo) first-order. Make sure that that “CVSim –  $k_f = 10000$ ” is the active simulation and click on **Simulation -> Copy** (  ), create a new **CV-Simulation Document** as described in 1.1. and click twice on **Simulation -> Paste** (  ) to paste two copies of “CVSim –  $k_f = 10000$ ” into the new simulation document. Then click on **Simulation -> Edit Properties** (  ), go to the **Chemical Reactions** page and click on the left-most index field associated with the first-order reaction

Chemical Reaction	Keq	$k_f$	$k_b$
Red = P	10000	10000	1

Cancel  
 Edit Reaction  
 Remove Reaction  
 Edit Fitting Options

Select **Edit Reaction** and modify the reaction template as follows

**Add Chemical Reaction** ✖

Red + A = P + B

OK Help Cancel

Alternatively, select **Remove Reaction** to remove “Red = P” and enter the new reaction “Red + A = P + B” from scratch as described in 1.6.

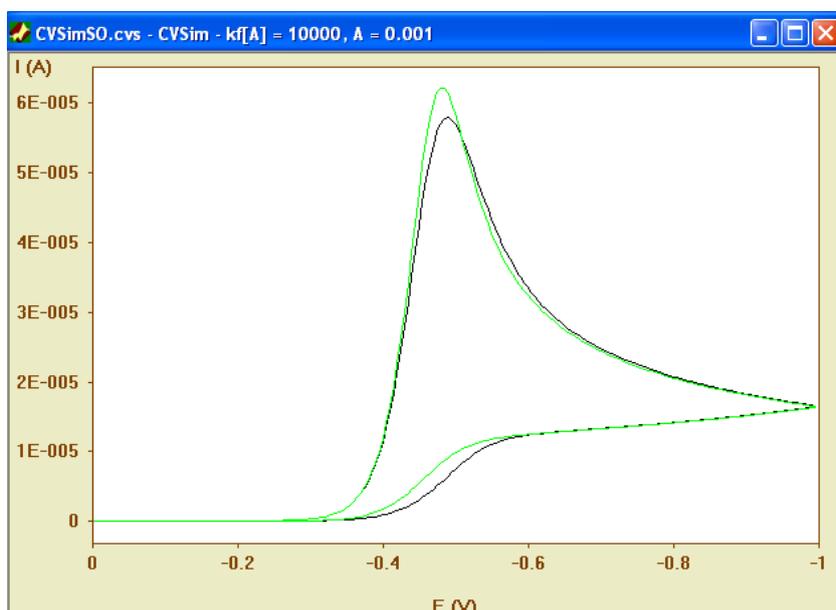
Close with **OK** and enter the following values for  $K_{eq}$ ,  $k_f$  and the analytical concentrations,  $C_{anal}$  (mol/l).

	Chemical Reaction	Keq	kf	kb
1	Red + A = P + B	10000	1E+006	100
2				
3				
4				
5				

	Species	D (cm <sup>2</sup> /s)	Canal (mol/l)	Cinit (mol/l)
1	Ox	1E-005	0.001	0.001
2	Red	1E-005	0	0
3	A	1E-005	0.01	0.01
4	P	1E-005	0	0
5	B	1E-005	0	0

The values have been selected such as to make  $k_f[A]=10000$  where  $[A]$  is an abbreviation for the analytical concentration of A. A value of 10000 was also used for first-order rate constant in “CVSim – kf = 10000”. Go to the **Simulation Parameters** page and enter “CVSim - kf[A] = 10000, A=0.01” as simulation name. Running the simulation reveals that both simulations (the first-order one “CVSim – kf = 10000” and the second-order one “CVSim - kf[A] = 10000, A=0.01” ) exhibit identical current curves within an error level smaller than about 0.5%. A tenfold excess of species A is therefore enough to obtain pseudo-first order conditions for the selected scan rate. However, it is easy to verify that the effect of the second-order reaction can no longer be neglected if the ratio of the analytical concentration between Ox and A tends towards 1 or becomes even smaller. For instance  $k_f=10^7$  and  $[A]=0.001$  yields the following result (black curve)



while the green curve refers to the first-order mechanism “CVSim – kf = 10000”.

### 1.8. Deleting a simulation object

The **active simulation** can be removed from the (active) simulation document by clicking on **Simulation ->**

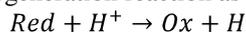
**Delete** or on **Simulation -> Cut** (  ). In the latter case the simulation is moved to the clipboard and can be re-pasted again.

### 1.9. Adding another chemical reaction

Remove the simulation object associated with the second-order mechanism by activating

“CVSim - kf[A] = 10000, A=0.01” and clicking on **Simulation -> Delete** . Only “CVSim – kf = 10000” should

be displayed now on the screen. Then click on **Simulation -> Duplicate** (  ) and go to the **Chemical Reactions** page. Now we are going to investigate how the current curve changes if *Red* does not only undergo a first-order decomposition reaction but also a catalytic regeneration reaction as expressed in the following equation



This reaction is added by clicking on the left-most index field associated with the first empty line in **Chemical Reaction**

	Chemical Reaction	Keq	kf	kb
1	Red = P	10000	10000	1

Select **Add new Reaction** and enter the chemical reaction in the following way

**Add Chemical Reaction** ✖

Red + H+ = Ox + H

OK Help Cancel

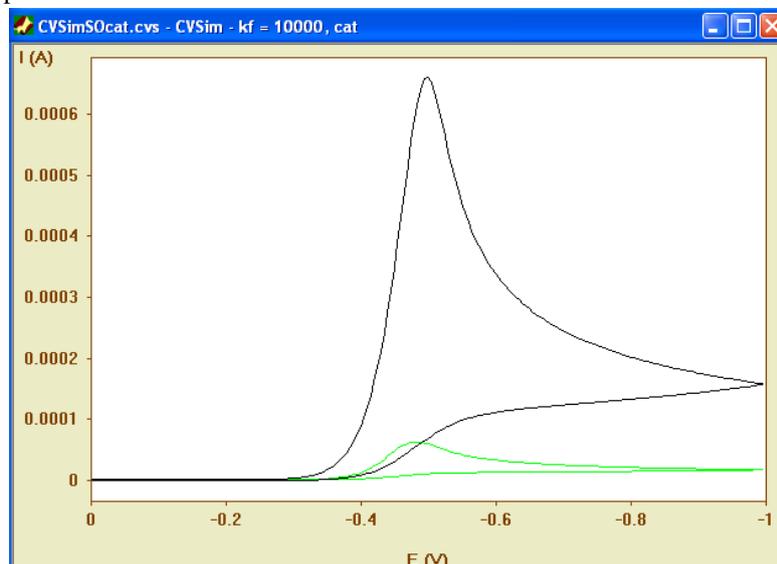
Return with **OK** and enter the following values for  $K_{eq}$ ,  $k_f$  and the *analytical concentrations*,  $C_{anal}$  (mol/l).

	Chemical Reaction	Keq	kf	kb
1	Red = P	10000	10000	1
2	Red + H+ = Ox + H	10000	1E+008	10000
3				
4				
5				

	Species	D (cm <sup>2</sup> /s)	Canal (mol/l)	Cinit (mol/l)
1	Ox	1E-005	0.001	0.001
2	Red	1E-005	0	0
3	P	1E-005	0	0
4	H+	1E-005	0.01	0.01
5	H	1E-005	0	0

Running the simulation (denoted as “CVSim – kf = 10000, cat”) yields the black current curve in the following picture:



In this way any number of chemical or charge-transfer reactions can be added to the mechanism. Note that the lists of reaction equations appearing under **Chemical Reaction** and **Charge-Transfer Reaction** will be automatically extended if the last line has been filled with a reaction equation.

## 2. Retrieving the coordinates of current points, zooming the screen display

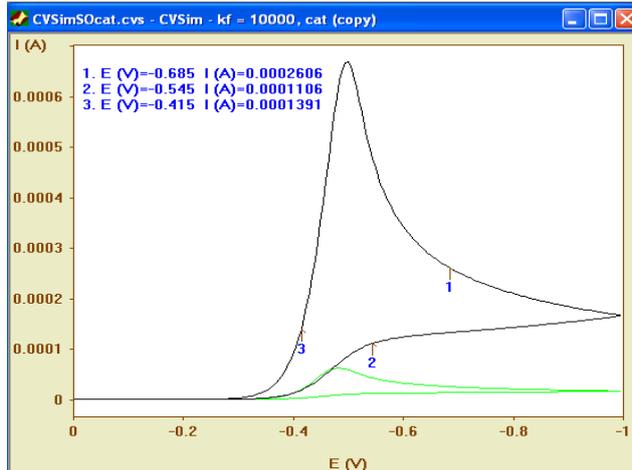
### 2.1. Retrieving the actual position of the mouse cursor

The actual position of the tip of the mouse cursor is displayed as xy-couple in the status bar

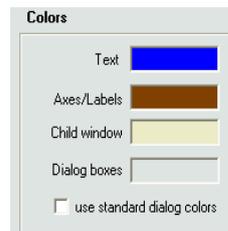
X: -0.4568 Y: 0.0004248

provided **View -> Status Bar** is check marked.

The coordinates of the current point (of the active simulation!) which is closest to the tip of the mouse cursor are displayed on the screen as shown in the picture on the left-hand side when executing a double click with the left mouse button. The command can be repeatedly applied



The coordinates referring to each click are displayed using the color settings of **Text** in **Colors** available on the **Preferences** page. This page is raised by clicking on



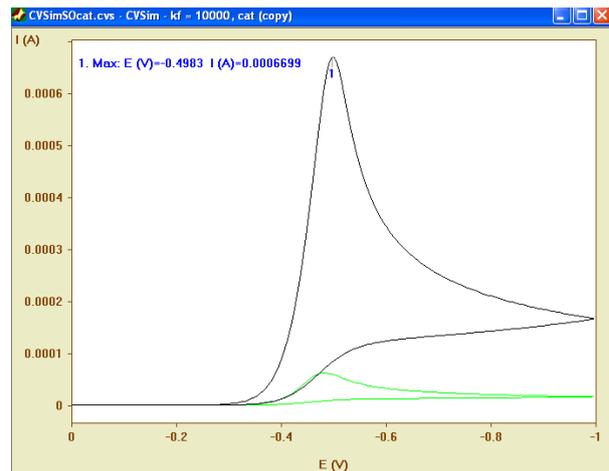
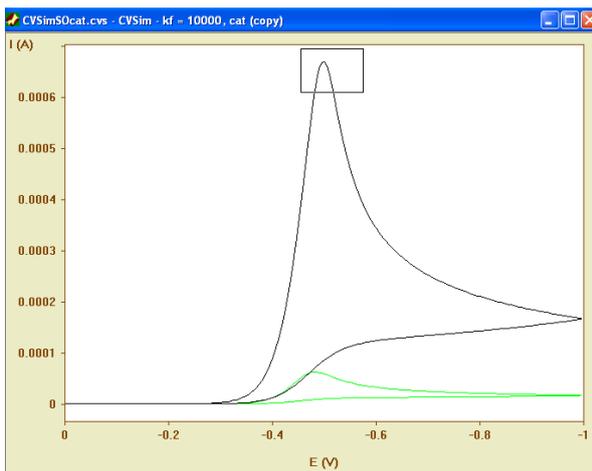
**View -> Preferences** (  )

The text can be removed from the display by clicking on **View -> Refresh** (  ).

### 2.2. Retrieving the coordinates of current peak maxima or minima

The coordinates of current peak maxima or minima are retrieved by clicking on **View -> Active Simulation ->**

**Show Min/Max-Info** (  ). Then press down the left mouse button and draw a rectangle around the region where the minimum/maximum is localized as shown in the picture on the left-hand side. After releasing the left mouse button the coordinates of the minimum/maximum (if any) are plotted on the screen as shown in the picture on the right-hand side.

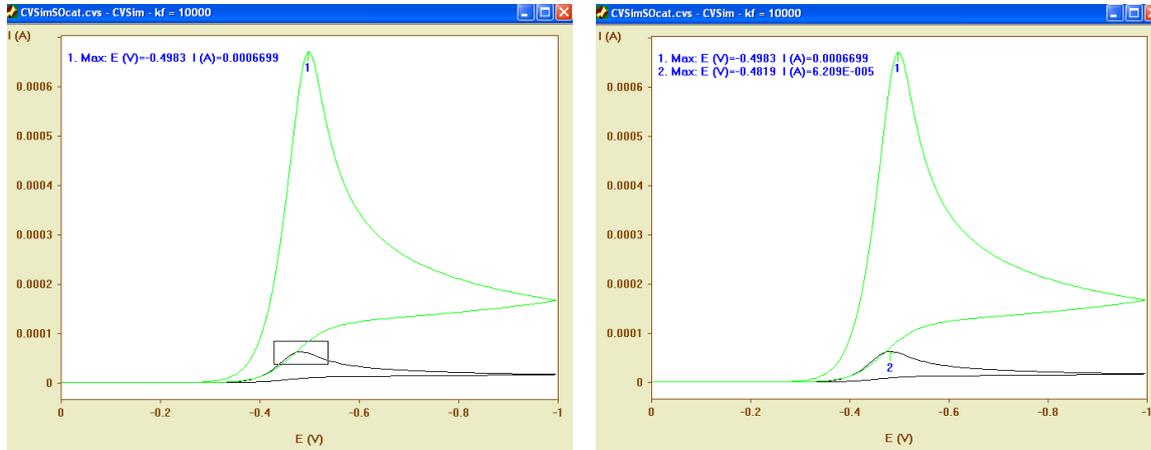


The text can be removed and its default color can be modified as described above in 2.1.

The command can be repeatedly applied in order to accomplish that the coordinates of all peak currents are shown on the screen. Proceed as follows if you want to compare the peak current of the active simulation with that of the inactive simulation. After having retrieved the peak current for “CVSim – kf = 10000, cat” as

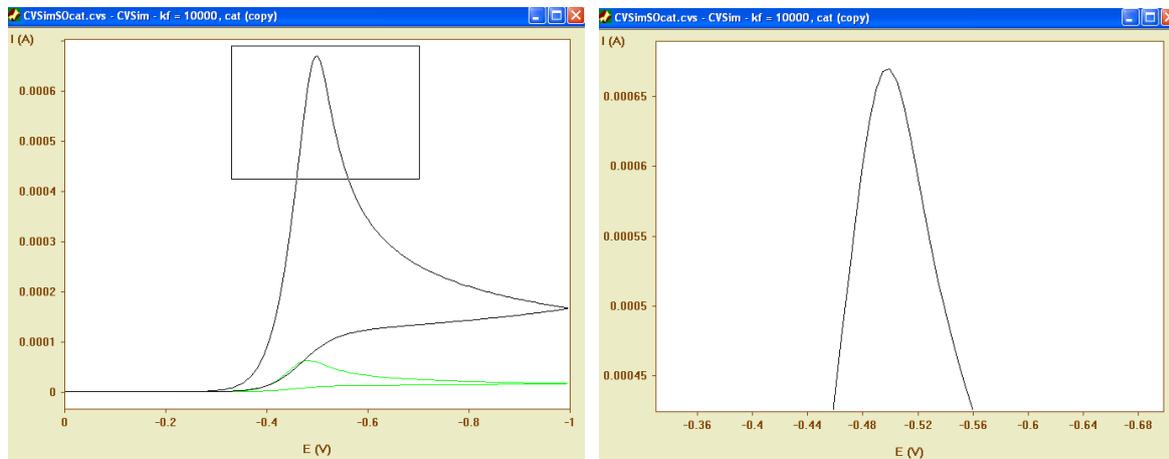
described above, click on **View -> Activate Next Simulation** (  ) in order to accomplish that “CVSim – kf = 10000” becomes the active CV. This is necessary because the command **View -> Active Simulation -> Show**

**Min/Max-Info** () works only with the current curve of the active simulation. Use this command as described above for drawing a rectangle around the region where the peak current of “CVSim – kf = 10000” is localized (see the picture on the left-hand side). After releasing the left mouse button, the coordinates of both peaks are plotted as shown in the picture on the right-hand side.



### 2.3. Zooming and unzooming the screen display

The screen display can be zoomed by clicking on **View -> Zoom** () , then press down the left mouse button and draw a rectangle around the region which is to be zoomed as shown in the picture on the left-hand side. This region is expanded to “full screen” as shown in the figure on the right hand side after releasing the right mouse button



The **View -> Zoom** () – command can be repeatedly applied up to 9 times. The zooming effect can be undone by clicking on **View -> Unzoom** () .

If the original screen display has been zoomed  $n$ -times the **View -> Unzoom** () -command must also be applied  $n$ -times to re-establish the original screen display.

### 3. Saving the simulation document, saving the screen display, exporting and importing simulations

#### 3.1. Saving the simulation document

All simulations involved in a simulation document can be saved by means of a standard Windows file dialog that appears when clicking on **Document -> Save** (  ) or **Document -> Save As**. The first command works “quiet” using the default path for saving the simulation document. The second command enables the user to save the document with a new name. **Document -> Save As** is used instead of **Document -> Save** if a new document (with an empty default path) is saved for the first time.

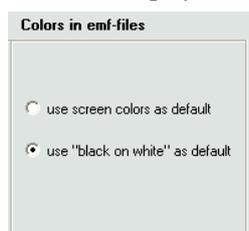
All chemical parameters and all simulation parameters (including the current curve) but not the settings for the screen display such as colors, fonts etc. are saved for each simulation.

At this point we recommend that the user saves the simulation document obtained so far using the name “CVSimSOcat.cvs”. After saving, this name becomes the document’s name shown in the window’s title bar (see the previous pictures).

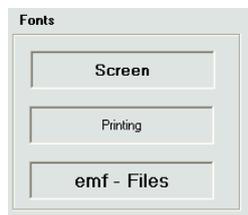
Note that cvs-files are saved in a binary format which cannot be handled by any third-party software.

#### 3.2. Saving the screen display

The graphics of the screen display can be saved in enhanced Windows metafile (emf-) format by clicking on **Document -> Save Screen Display** (  ). The screen display can be saved either in “black and white” or using the actual display colors (except the child window’s background color which is always saved in white).



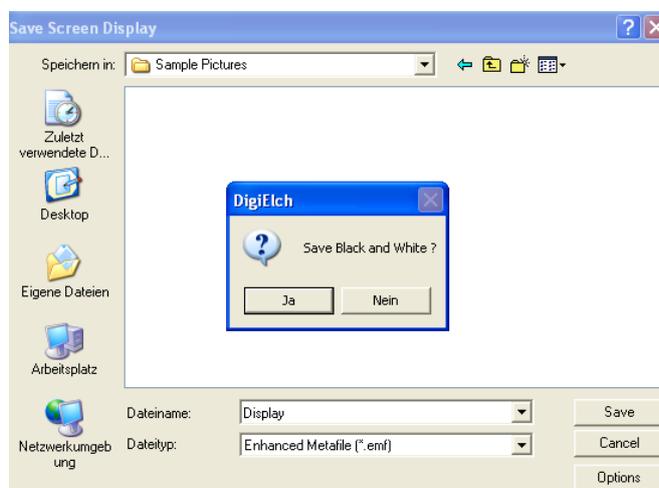
Whether the first option or the second one is used depends on the default settings of **Colors in emf-files** which can be adjusted by clicking on **View -> Preferences** (  )



The default type and size of the font used for labeling the axes in the emf-file can be adjusted independently of the screen font by means of a standard Windows font dialog that appears when clicking on **emf-Files**. The **Fonts** settings are available on the

**Preferences** page raised by clicking on **View -> Preferences** (  )

The **Document -> Save Screen Display**-command opens a slightly modified standard Windows file dialog.

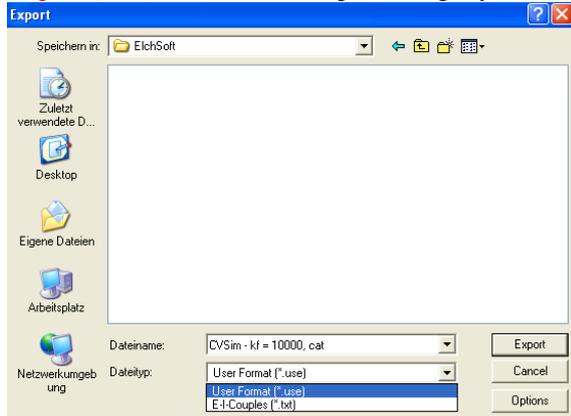


Clicking on the button **Options** enables the user to select whether the screen display is saved in “black and white” or using the actual screen colors. This selection applies only to the actual operation and does not overwrite the default settings of **Colors in emf-files** on the **Preferences** page.

### 3.3. Exporting a simulation

The current curve of the active simulation can be exported in ASCII-format by applying the **Simulation ->**

**Export** (  ) – command. It opens a slightly modified standard Windows file dialog



The two different export options are described in the following:

#### 3.3.1. Export Option: Use Format (\*.use)

Pressing directly the **Export** button saves the current curve, the **Experimental Parameters** (i.e. the parameters for **Scan, Pre-Equilibrium, Geometry, Diffusion** and **Experimental Conditions**) as well as the **Species Parameters** (**Species concentrations and boundary conditions**) shown on the **CV-Properties** dialog (but **not** the **Chemical Reactions and Preferences**) in an ASCII format that can be re-imported into *DigiElch*. Note that the *key words* are identical with the parameter names on the **Simulation Parameters** page shown of the **CV-Properties** dialog

raised by clicking on **Simulation -> Edit Properties** (  ).

Thus, for instances, when exporting the simulation “CVSim – kf = 10000, cat” (contained in the simulation document that has been saved as “CVSimSOcat.cvs” in 2.1.) the following data are written to the use-file (the left-hand side shows the data actually written to the use-file, the right-hand-side the general structure of the use-format)

```
source program: DigiElch for Windows
program version: 3.0
file type: CV
```

```
experimental parameters:
Pre-Equilibrium: smart
Diffusion: Semi-Infinite 1D
Geometry: Spherical (Hg)
Mass (mg): 4
Ru (Ohm): 0
Cdl (F): 0
Temp. (K): 298.2
Potential steps (V): 0.005
Estart (V):0
Segment: 1
Eend (V): -1
v (V/s): 10
Segment: 2
Eend (V): 0
v (V/s): 10
```

```
species parameters:
[Ox] (M/l): 0.001
[Red] (M/l): 0
[P] (M/l): 0
[H+] (M/l): 0.01
[H] (M/l): 0
```

```
experimental CV-data:
number of E (V), I (A) couples: 400
-0.005 , 2.8397268E-011
-0.01 , 3.4379793E-011
-0.015 , 4.1844406E-011
:
```

#### **DigiElch CV-Header**

“program version” means here the version of the use-format which is “3.0” and may be different from the version of *DigiElch*.

#### **experimental parameters:**

```
key_word_1: Value_1
key_word_2: Value_2
:
:
etc.
```

#### **species parameters:**

```
[name of species_1] (M/l): Canal_1
[name of species_2] (M/l): Canal_2
:
:
```

#### **experimental CV-data:**

```
number of E(V), I (A) couples: N
E_1 , I_1
E_2 , I_2
etc.
```

Experimental and Species Parameters can be modified or excluded from being exported using the dialog box that appears when pressing the **Options** button:

Segment	Estart (V)	Eend (V)	v (V/s)
1	0	-1	10
2	-1	0	10
3			
4			

Number	Species	Amalgam	Canal (m/l)
1	Ox	NO	0.001
2	Red	NO	0
3	P	NO	0
4	H+	NO	0.01

Note the difference between an empty input field and an input field where "0" has been entered. In the example shown left no entry is produced in the use-file for the double layer capacity,  $Cdl (F)$ , and for the temperature,  $Temp.(K)$ , while  $Ru (Ohm) = 0$  is explicitly written to the file.

```

source program: DigiElch for Windows
program version: 3.0
file type: CV

experimental parameters:
Pre-Equilibrium: smart
Diffusion: Semi-Infinite 1D
Geometry: Spherical (Hg)
Mass (mg): 4.1
Ru (Ohm): 0
Potential steps (V): 0.005
Estart (V):0
Segment: 1
Eend (V): -1
v (V/s): 10
Segment: 2
Eend (V): 0
v (V/s): 10
:
:

```

In the above example, a mercury mass of  $4.1mg$  is written to the use-file while the current curve contained in this file refers to  $4.0mg$ . Why does *DigiElch* provide an option for falsifying parameter values before exporting them? The answer is quite simple: use-files are mainly intended for fitting purposes. In such a situation it makes thoroughly sense to investigate the effect of a systematic parameter error on the thermodynamic and or kinetic constants retrieved by the fitting routine. In other words, falsified use-files could be used to mimic experimental data files where some experimental parameters such as electrode size or species concentrations are not exactly known. Subjecting such files to data fitting provides an easy way to investigate how an uncertainty in some experimental parameters is passed to the thermodynamic and or kinetic constants we are interested in.

### 3.3.2. Export Option: E-I-couples (\*.txt)

Data exported in this way cannot be re-imported into *DigiElch*. The purpose of this export option is to export the current curve in a format that can be easily handled by third-party presentation software. For this purpose a few formatting options are provided.

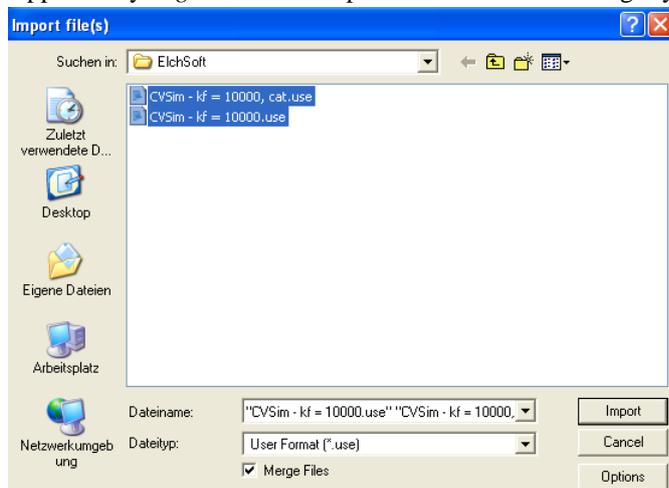
By default (i.e. when selecting this export filter and pressing directly the **Export** button in the Windows file dialog box shown in 3.3.) the current curve is exported in the form of voltage-current couples using the number-format and the separator selected in **Exporting Data** available on the **Preferences** page which is raised by clicking on

**View -> Preferences** ( ).

This selection can be temporarily overwritten (without changing the default settings in **Exporting Data**) by clicking on the **Options** button in the Windows file dialog box shown in 3.3.

### 3.4. Importing simulated or experimental CVs

Two import commands are available. The first one (**Simulation -> Import (\*.use)** ) can be used for importing CV-simulations or experimental CVs stored in use-format (see 3.3.1.). The second one (**Simulation -> Import (\*.txt, \*.dat)**) can be used for importing experimental CVs produced by a few third party instruments supported by *DigiElch*. Both import commands raise a slightly modified Windows file dialog box:



The available import filters depend on the actual version of the *DigiElchImport.dll*.

When the **Merge Files** button is checked, the imported CV-objects are merged (added) to those already present in the active simulation document. When de-activated, all simulations in the active simulation documents are deleted before importing the file(s).

Clicking the **Options** button enables the user to decide whether the sign of the cathodic/anodic current is changed by multiplying the current values with -1. This is necessary only when importing files where the sign convention used in the file is different from that expected by *DigiElch*. (In *DigiElch*, the cathodic current is assumed to be positive).

**Do not use this option for importing standard use-files produced by *DigiElch*!!**

#### 3.4.1. Importing data files in use-format

When importing use-files (see 3.3.1), the **Experimental** and **Species Parameters** of the active simulation serve as default values for the imported object. These values are overwritten only if an entry for this parameter is explicitly found in the use-file.

```
source program: DigiElch for Windows
program version: 3.0
file type: CV
```

```
experimental CV-data:
number of E (V), I (A) couples: 400
-0.005 , 2.8397268E-011
-0.01 , 3.4379793E-011
-0.015 , 4.1844406E-011
:
:
```

The **minimum** use-format accepted by *DigiElch* (shown on the left-hand side) requires the ***DigiElch* CV-Header**

followed by the following two lines:

```
experimental CV-data:
number of E(V), I (A) couples: N
```

where **N** is the number of voltage-current couples representing the current curve. The numbers must be in *point format* and separated by a *comma*.

When re-importing a file in **minimum** use-format (containing only the current curve), the **Experimental** and **Species Parameters** for the imported object are exclusively taken from the active simulation. **The main purpose of the minimum use-format is to offer an easy and straightforward way for importing data produced by third-party instruments into *DigiElch*. It is up to the user to ensure (by entering appropriate values for the active simulation) that these parameters are in a reasonable relationship to the imported current curve.**

#### 3.4.2. Importing ASCII-files from third-party instruments supported by *DigiElch*

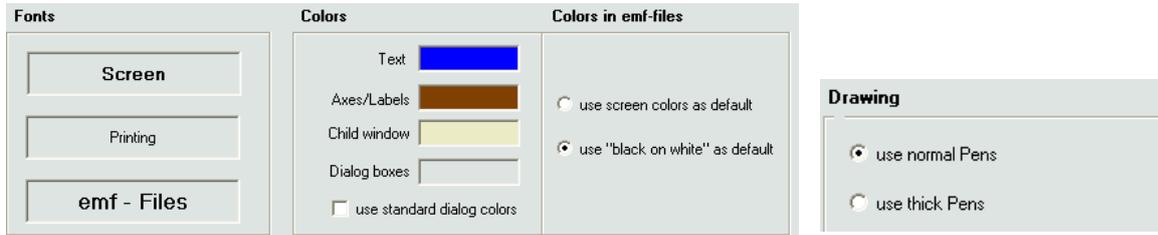
Most of the import filters provided for this purpose extract only the experimental current curve from the txt- or dat-file. As in the case of importing files in **minimum** use-format the **Experimental** and **Species Parameters** for the imported object are exclusively taken from the active simulation and it is up to the user to ensure (by entering appropriate values for the active simulation) that these parameters are in a reasonable relationship to the imported current curve.

### 4. Customizing colors, fonts and the drawing of the cyclic voltammetric current curve

The options for customizing colors, fonts and the drawing of the screen display are split into two groups: The **first group** involves options which apply to all windows associated with a CV-simulation document no matter whether CV-current curves, concentration profiles or fitting objects are displayed. The **second group** applies only to the display of the cyclic voltammetric current curves.

#### 4.1. Customizing options applying to all windows

These options are compiled on the **Preferences** page which appears by clicking on **View -> Preferences** (  ).



The options for **Colors in emf-files** have already been described in 2.2. The remaining options work as follows:

##### Fonts

The default font and its size used for labeling the axes can be adjusted independently for screen display, printing and for the saving of the screen graphics in emf-format by means of the standard Windows font dialog that appears when clicking on the associated text field.

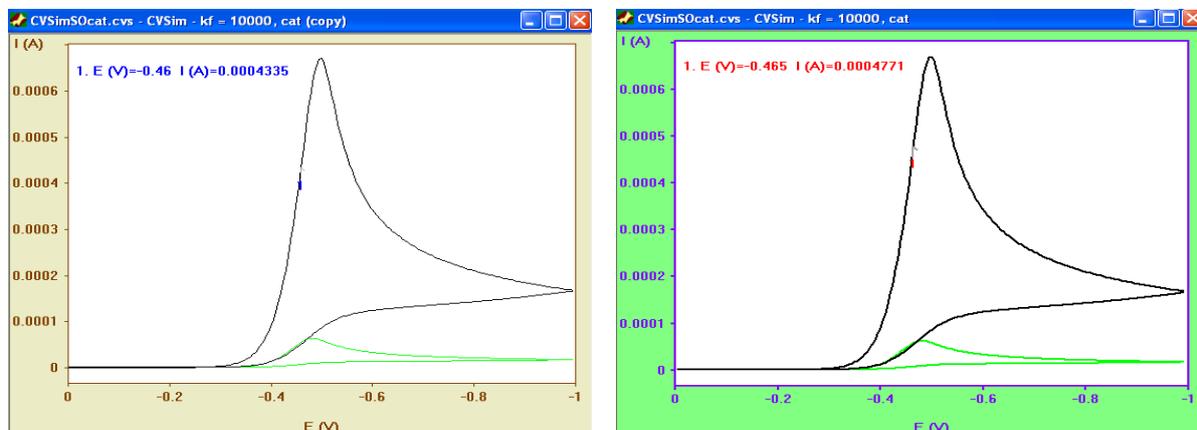
##### Colors

The default colors for drawing the info-text, for labeling axes as well as the child-window's background color and the color of dialog boxes can be adjusted by means of the standard Windows color dialog box that appears when clicking on the associated color field. The color shown in the field associated with **Dialog boxes** is only used if **use standard dialog colors** has not been selected. Otherwise, the color settings of the operating system are used for all *DigiElch*'s dialog boxes. Note that changing the color settings for **Dialog boxes** and **Child window** takes effect only when creating/opening a new dialog box/child window.

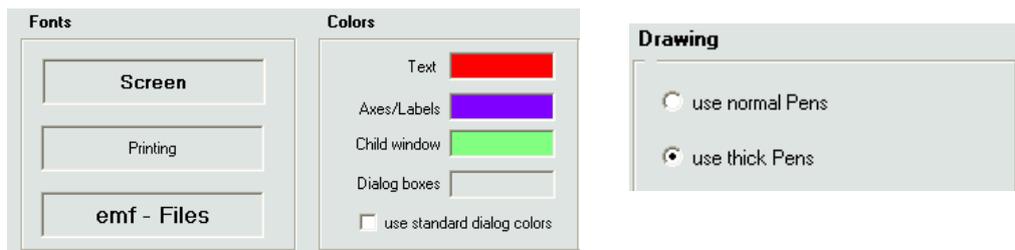
##### Drawing

This selection decides whether a normal or a thick pen is used for printing, storing emf-files and drawing the screen display.

Example:



**left-hand side:** appearance of the screen display using the **Fonts-**, **Colors-** and **Drawing-**settings shown above  
**right-hand side:** appearance of the screen display using the **Fonts-**, **Colors-** and **Drawing-**settings shown below

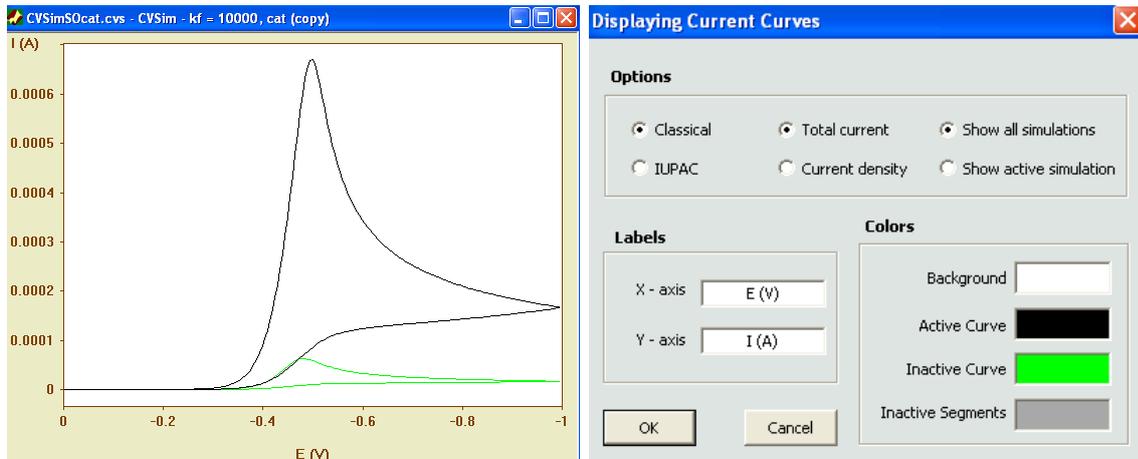


##### Resetting the default colors:

The default colors can be reset by clicking on **View -> Reset Default Colors** in *DigiElch*'s start menu. The latter is active only immediately after starting *DigiElch* or when closing all child windows.

#### 4.2. Customizing options applying only to the display of the cyclic voltammetric current curves

Clicking with the right mouse button while the mouse cursor is localized over the window showing the CV-current curve opens the dialog box shown on the right-hand side. The screen display produced with these **Options**, **Labels** and **Colors** is shown in the picture on the left-hand side:



#### Options

- **Classical/IUPAC**  
if **Classical** is selected negative potentials are drawn from left to right and the cathodic current is positive. Otherwise positive potentials are drawn from left to right and the cathodic current is negative
- **Total current/Current density**  
Either the total current or the current density is plotted.
- **Show all simulations/Show active simulation**  
Either the current curves of all simulations involved in the simulation document or only that of the active simulation is plotted.

#### Colors

The default colors for drawing the background, the active CV, the inactive CV and the inactive cycles (segments) of the active CV can be adjusted by means of the standard Windows color dialog box that appears when clicking on the associated color field.

#### Labels

The default labeling for the x- and y-axis can be modified by changing the text in the associated text field. Note, however, that the label " $I$  (A/cm<sup>2</sup>)" is always used if **Current density** is selected.

The effect of the settings in **Options**, **Labels** and **Colors** can be summarized by comparing the screen display referring to the following settings with that shown above

