Lesson 2:

The „Lesson2.zip"- archive contains 4 files (**File1.use** to **File4.use**) in minimum use-format. It is assumed the 4 files represent 4 CVs measured with different scan rates using an instrument that does not support *DigiElch's* use-format. That means the files contain only the current curve in the form of potential-current couples in the format required by *DigiElch* (numbers in "point format" separated by a comma). In other words, the data in the files may look as follows:

0.299 , -2.0072069E-007
0.298 , -2.7082669E-007
0.297 , -6.6917692E-008
0.296 , 7.8437734E-010
0.295 , 2.0400111E-007
0.294 , -1.3490491E-007
0.293 , 2.0396988E-007
….

etc.

It is further assumed that the sign of the current is in agreement with *DigiElch*'s convention whereupon the cathodic current is positive and the anodic current is negative. (see18. how to proceed if the opposite sign convention is used in the data files).
In that case it is sufficient to add the *DigiElch* header manually to each file in order to make the files compatible with *DigiElch's* minimum use-format. After this operation each file looks similar as **File1.use** partly shown in the following example:

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

experimental CV-data:
number of E (V), I (A) couples: 1200
0.299 , -2.0072069E-007
0.298 , -2.7082669E-007
0.297 , -6.6917692E-008
0.296 , 7.8437734E-010
0.295 , 2.0400111E-007
0.294 , -1.3490491E-007
0.293 , 2.0396988E-007
….
etc.

Note that the correct value for "number of E (V), I (A) couples:" must be indicated after the colon! The data will not be correctly imported if this number is smaller than the actual number of data couples stored in the file.

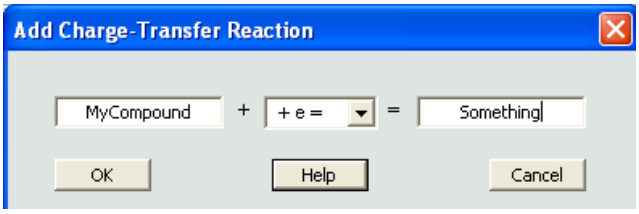
The user knows that *0.001 mol* of "MyCompound" was measured at a mercury drop electrode (the average mass of the mercury drop amounted to *4 mg*) using scan rates of *1 V/s* (File1.use), *3 V/s* (File2.use), *10 V/s* (File3.use) and *30 V/s* (File4.use). The user is sure that "MyCompound" does not undergo site reactions with the solvent or the supporting electrolyte. It is therefore reasonable to investigate how well the experimental results can be reproduced on the basis of a simple charge transfer mechanism. For this purpose we make use of *DigiElch's* non-linear regression procedure in the following way:

When working through the lesson, please, keep in mind that a few menu commands are disabled in the not activated program running as trial installation.

1. Start *DigiElch*, click on New and create a new CV-Simulation Document

2. It is important to emphasize that the active simulation plays the role of a template simulation object when importing experimental data files into *DigiElch*. That means, an Experimental Parameters defined in the active simulation is overwritten by an imported one only if an entry for this particularly parameter is explicitly found in the data file. (Here and in the following Experimental Parameters denotes the parameters shown in the dialog box of point 8.) For this reason we generate a template mechanism that enables us to enter all Experimental Parameters which are explicitly known and which apply to the majority of experimental data files. In the above example this is the analytical **concentration, Canal (m/l) = 0.001**, of "MyCompound", the fact that *DigiElch's* **Pre-Equilibriu**m option should be set at **disabled** or **smart** (no site reactions) and that a **4-mg mercury drop electrode** was used. (The scan rate does not matter in the moment because it differs from file to file. This info must be past to *DigiElch* in a different way described in 8.). Click on Data Fitting->Prepare Fitting Project for activating the Data Fitting Menu and try to start with a simple charge-transfer mechanism.

3. Go to Chemical Reactions in the appearing CV-Properties page and enter any mechanism containing the species names you want to use later when fitting the data. It should be emphasized that this mechanism needs not to be the one later used in the fitting project – only the same names must be used for all species which must be imported during data fitting to ensure that the correct analytical concentrations are used by the fitting routine. In the present case a simple charge transfer reaction is entered (click on in front of Charge Transfer Reaction to get help or work through Lesson0 if you do not know how reactions are added in *DigiElch*)

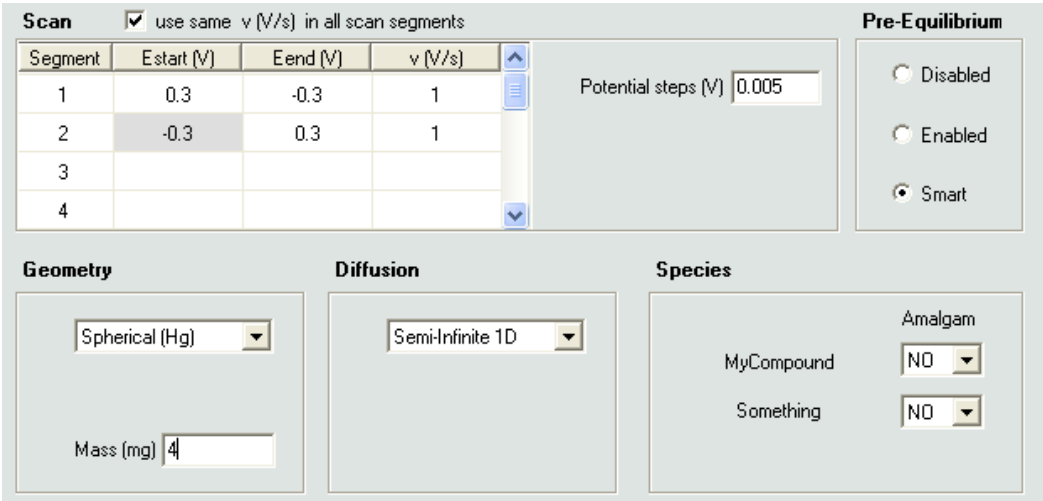


(Of course, you may use more meaningful names).

4. Click on **OK** and enter the known **analytical concentration** for "MyCompound"

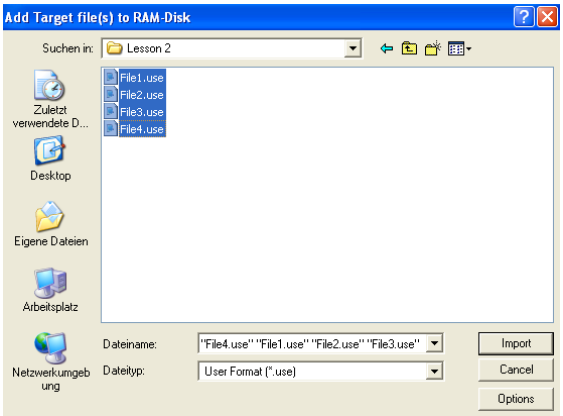
	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	MyCompound	1E-005	0.001	0.001
2	Something	1E-005	0	0
3				

5. Go to Simulation Parameters and enter the known **electrode geometry** and **mercury mass**. Set the **Pre-Equilibrium** option to "**Smart**". Also make sure that "normal" CVs are simulated by activating **Use the same value of v(V/s) in each scan segment**.



The **Scan** itself and the selected **Potential steps (V)** need not to be correct because this data will be extracted from the experimental CVs stored in **File1.use** to **File4.use**.

6. Close the CV-Properties dialog and click on Data Fitting->Add Target Curves to RAM-Disk. Select **File1.use – File4.use** as shown below and click on **Import**.

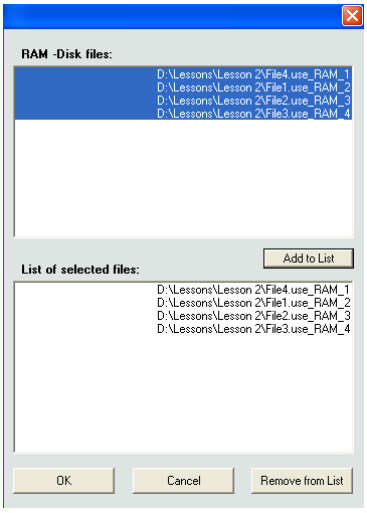


Note that these files may be localized at a different place on your computer.

Clicking on the **Options** button enables the user to add an identification string to the name of each selected files. This is useful for a better distinction of RAM-Disk files added to the RAM-Disk from different directories.

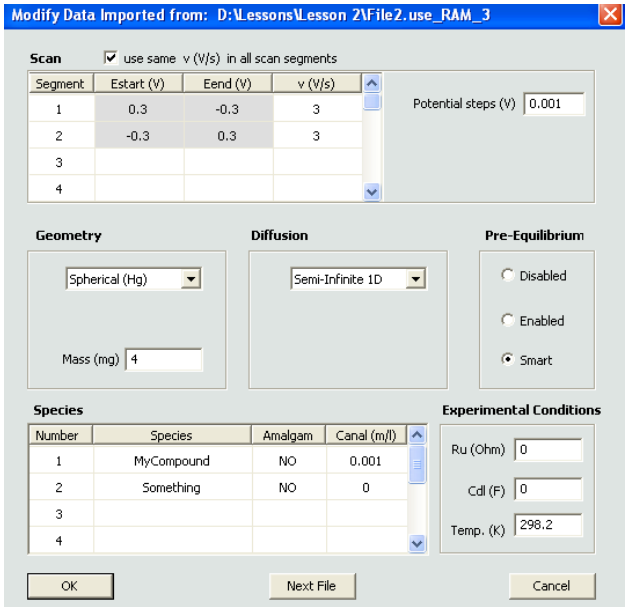
The files are now internally saved in a RAM-Disk that serves as the pool of files which can be potentially used by the fitting procedure. The files which are really used are selected in the following way

7. Click on Data Fitting->Select Data Target Curves form RAM-Disk ( ), select the four files and click on **OK**



Note that an extension of the form **_RAM_index** is added to each file name to avoid the occurrence of identical file names if equally named files (localized in different directories) would be added to the RAM-Disk.

8. Now you need to add the experimental parameters which are specific for each file.



Click on Data Fitting->Modify Selected Target Files and enter the scan rate associated with each experimental data file. In the case of **File2.use** the value is *3V/s* and the dialog box should look as shown on the left.

Selecting **Use the same value of v(V/s) in each scan segment** makes that any change of **v(V/s)** is taken over for all scan segments. When deselecting this option *DigiElch* would be able to simulate CVs using an individual scan rate for each scan segment.

If the input for a file has been completed, click on **Next File.** Finish with **OK** if all files are done and if you are sure that *1 V/s* refers to **File1.use**, *3 V/s* to **File2.use**, *10 V/s* to **File3.use** and *30 V/s* to **File4.use**, respectively.

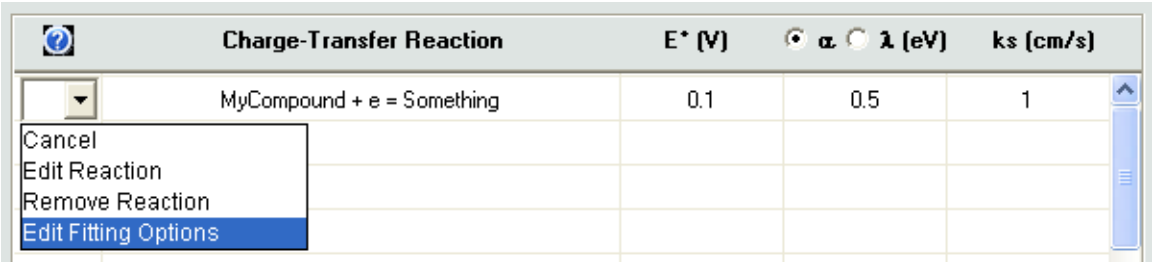
Note that step 8. needs not to be executed if the date would be in full use format (containing not only the current curve but also the complete set of experimental parameters stored in the file).

9. Optionally the menu command Data Fitting->Export Selected Target Files could be used now to export the modified data (file by file) either in full use-format or by overwriting the RAM-Disk files and saving the RAM-Disk content by means of the Document -> Save RAM-Disk command. If saved as use-files, it is recommended to assign a new name to these files to avoid the overwriting of the original data files. Quit with **Cancel** if all files have been exported.

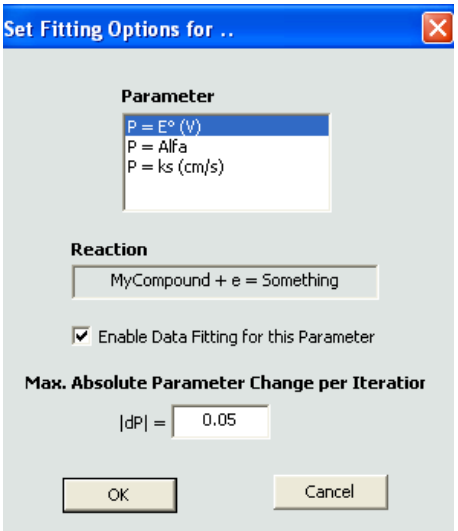
10. In the next step you need to specify which (electro-) chemical parameters are to be determined by the fitting procedure and which starting values are used. Enter the following starting parameters

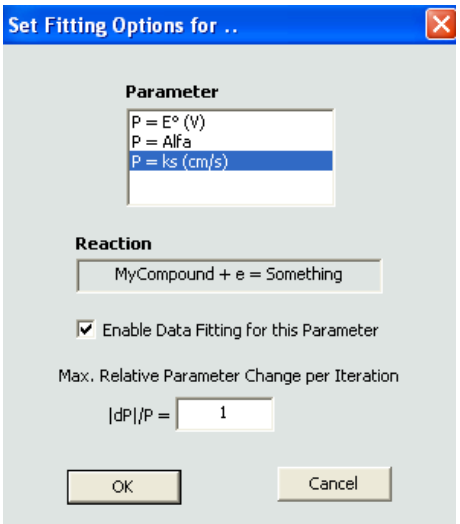
	Charge-Transfer Reaction	E° (V)	α λ (eV)	ks (cm/s)
1	MyCompound + e = Something	0.1	0.5	1
2				

Then click on the index field associated with this reaction and select **Edit Fitting Options** in the appearing combo box



and select the **standard potential**, E°(V), and **the heterogeneous rate constant,** ks(sm/s), for being optimized by the fitting procedure as shown in the following pictures





11. After leaving with **OK** the Chemical Reactions page should look now as follows

	Charge-Transfer Reaction	E° (V)	α λ (eV)	ks (cm/s)
1	MyCompound + e = Something	0.1	0.5	1
2				

Obviously, the parameters selected for being optimized are highlighted in magenta.

If also the **diffusion coefficient**, D(cm^2/s), of "MyCompound" is going to be optimized by the fitting procedure one should keep in mind that there is a parameter coupling (between the coupling between the standard potential and the ratio of the diffusion coefficients of the species involved in the redox-couple) that cannot be unravelled under certain conditions. (A more detailed discussion will be given in another teaching lesson). In most cases the fitting of diffusion coefficients **and** standard potential makes therefore sense only

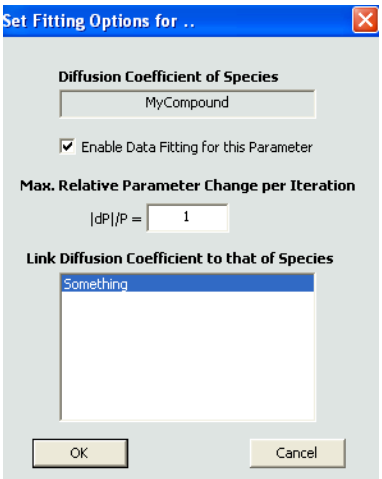
if the ratio of the diffusion coefficients is not changed by the fitting procedure. This can be accomplished by linking the diffusion coefficients of the underlying species as outlined in the following.
After entering a sensible starting value the **diffusion coefficient**, D(cm^2/s), of "MyCompound"

	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	MyCompound	2E-005	0.001	0.001
2	Something	1E-005	0	0

click on the index field associated with the Species "MyCompound"

	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
	MyCompound	2E-005	0.001	0.001
Cancel	Something	1E-005	0	0
Edit Fitting Options				

and enable the data fitting for the diffusion coefficient as shown in the following picture.



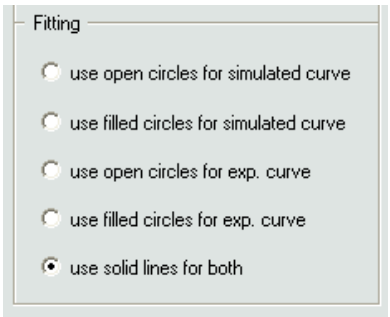
Also do not forget to link diffusion coefficient of the species "Something" with that of species "MyCompound"

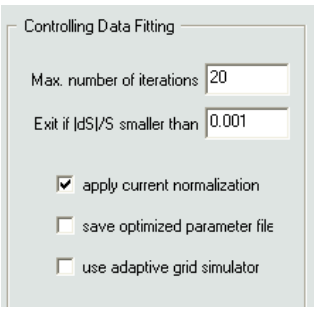
12. After leaving with the **OK** the Species area on the Chemical Reactions page should look now as follows

	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	MyCompound	2E-005	0.001	0.001
2	Something	2E-005	0	0
3				

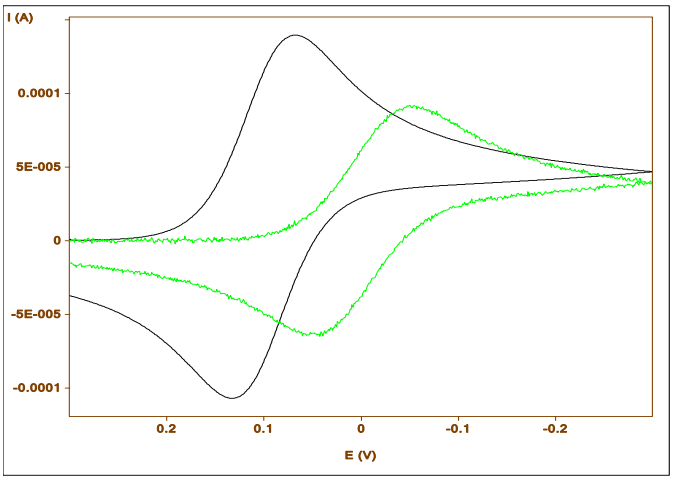
Analogously as in 10. the parameter optimized by the fitting procedure is plotted in magenta. The diffusion coefficient of "Something" which is linked with this parameter is drawn on a grey background. A grey background color indicates a "read-only" parameter which is set internally and cannot be edited by the user.

Before closing CV-Properties with **OK** go to Preferences and modify the default settings as follows



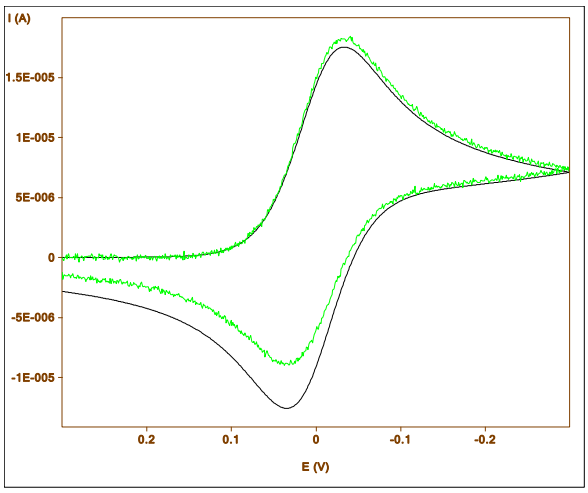


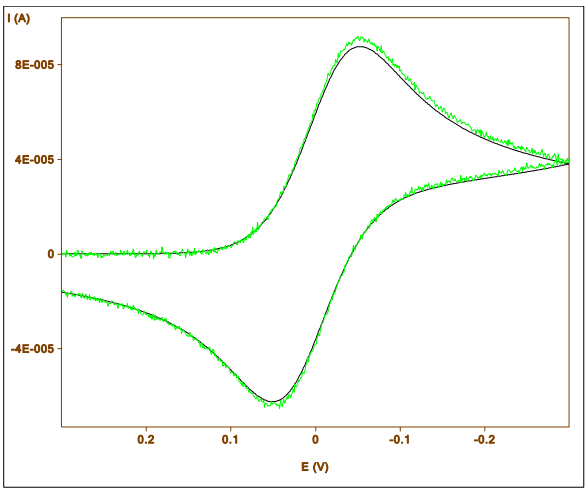
13. In order to see how sensible your starting values are it may be useful to import the first data file and to compare the result of the simulation (using the starting values) with the experimental current curve involved in that file. This is accomplished by the command Data Fitting->Compare Simulation with Experiment -> Show First Target Curve, Run & Compare ( )



The green (inactive) curve is the experimental CV imported from the first file (**File4.use**) the black (active) curve is that simulated with the starting parameters. The agreement is rather bad but sufficient for achieving fast convergence for a simple charge transfer-mechanism. Hence the fitting procedure can be started now.

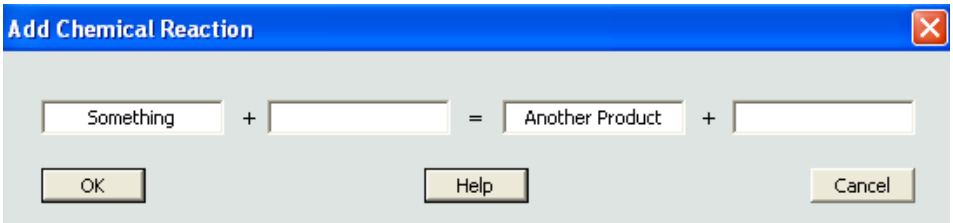
14. Click on Data Fitting->Run Fitting Procedure ( ) and watch how the program is trying to find the "best fit". Due to the bad starting parameters the fitting procedure needs 6 iterations for reaching the minimum standard deviation that can be obtained on the basis of a simple charge transfer mechanism. However, when comparing experimental and simulated CVs by means of the Data Fitting->Compare Simulations with Experiment-> Show Next Couple ( )-command it becomes clear that a reasonable agreement is achieved only for the data referring to the highest scan rate.





Results obtained on the basis of a simple charge-transfer mechanism: the left picture refers to **v(V/s) = 1** the right one to **v(V/s) = 30**

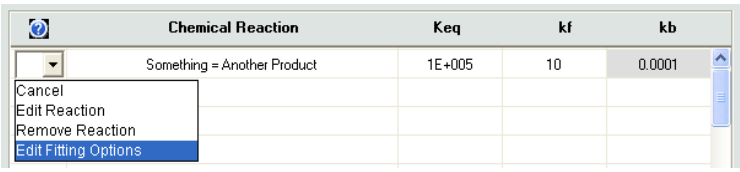
15. It is therefore likely that the reduced species "**Something**" undergoes a follow-up decomposition reaction leading to "**Another Product**". If this reaction is assumed to proceed as an irreversible first-order reaction the mechanism can be modified by clicking on Data Fitting->Mechanism & Starting Parameters ( ). Make sure that the Chemical Reactions page is activated and add the following homogenous chemical reaction (click on in front of Chemical Reaction to get help or work through Lesson0 if you do not know how reactions are added in *DigiElch*)

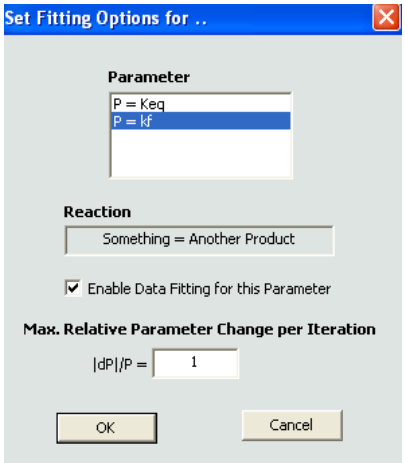


16. Close with **OK** and enter the following starting parameters

	Chemical Reaction	Keq	kf	kb
1	Something = Another Product	1E+005	10	0.0001
2				

A sufficiently large value of the equilibrium constant (**Keq** ≥10000) ensures that the effect of the follow-up reaction becomes independent of the diffusion coefficient of "Another Product" and independent of the particular value of **Keq**. That means it is exclusively governed by the homogeneous rate constant **kf** which is the only additional parameter that needs to be fitted, too. Consequently, click on the index field associated with that reaction, select **Edit Fitting Options** in the appearing combo box and enable **kf** for being optimized by the fitting procedure

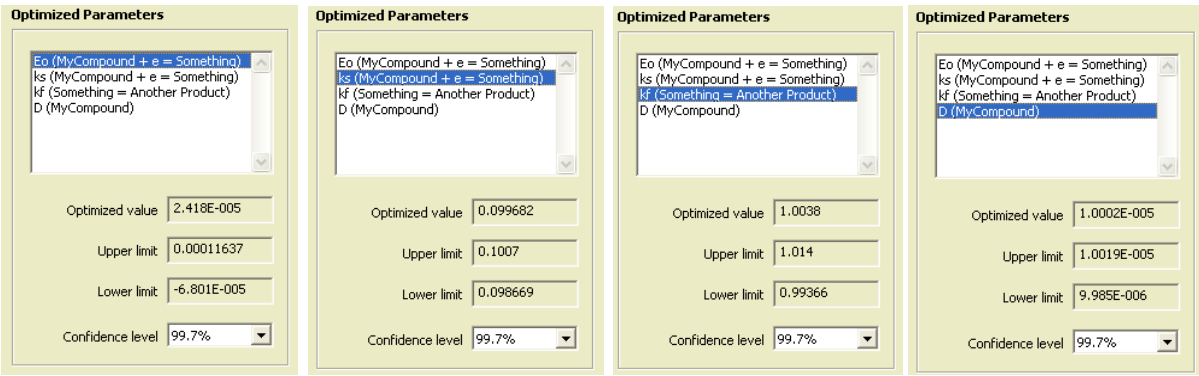




After leaving the dialog box on the right-hand side with **OK** the value of **kf** is plotted in magenta in order to visualize that this parameter will also be optimized now when restarting the data fitting.

Note that an analytical concentration of "Another Product" has not been defined in step 8. Consequently, the value defined in **Species** (it should be zero) is used for each experiment because no analytical concentration for "Another Product" will be imported during data fitting.

17. Close CV-Properties and re-do Data Fitting->Run Fitting Procedure. If the fitting procedure has terminated, apply the Data Fitting->Compare Simulations with Experiment-> Show Next Couple ( )-command again. Obviously, simulated and experimental CVs agree very well now for each scan rate. In "real life" the user may have to try several times as described above before getting satisfactory results. The good agreement is not surprising because the "experimental CVs" in **File1.use – File4.use** are not really experimental ones. They were obtained by adding a certain level of noise to simulated CVs obtained for the EC mechanism with $E° = 0V$, $ks = 0.1\ cm/s$, $kf = 1\ s^{-1}$ and $D = 10^{-5}\ cm^2/s$. Comparing the optimized parameter values with those used in the simulations reveals that the exact parameter values were retrieved by the fitting routine within the confidence interval effected by the noise level:

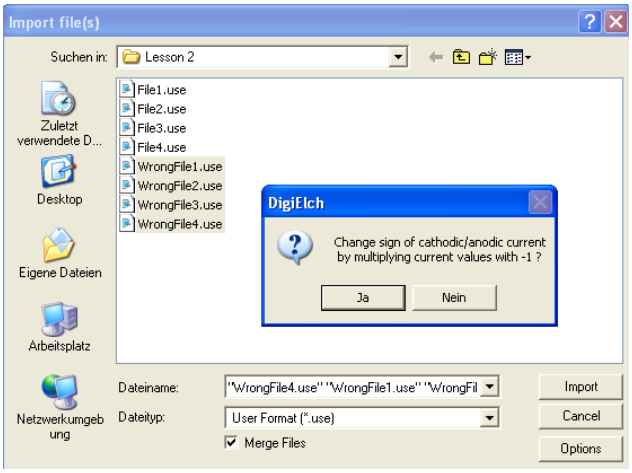


Setting up the fitting project if the current curve stored in the use-file has the wrong sign convention or if the data files are non-use files but data files from third-party instruments supported by *DigiElch*

18. The option for changing the sign of imported current curves and for the import of third-party data files is available only when working in the CV-Simulation Menu. For this reason, the experimental data files must be imported from within the CV-Simulation Menu and added to the RAM-Disk before activating the Data

Fitting Menu. In view of the discussion presented in 2. one should start again by entering a suitable simulation template before importing the data files. However, teaching efficiency is not the main topic of this lesson. Therefore it may be more instructive to see what the disadvantage is when starting with an empty (default) template. The following description assumes that we have data files in minimum use-format but the wrong sign convention. Nevertheless, the description applies analogously if third-party data files are used. In the latter case, the Simulation -> Import (*.use)-command in the following text must be replaced by the Simulation -> Import (*.txt, *.dat)-command.
Click on New and create a new CV-Simulation Document.

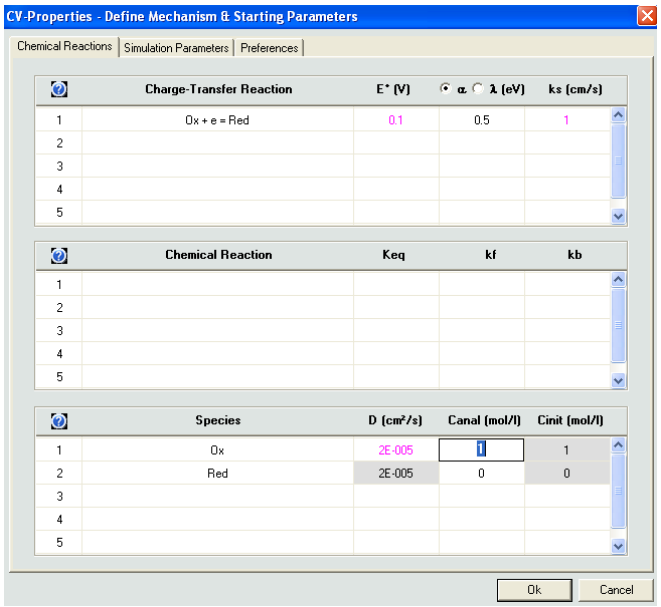
19. Click directly on Simulation -> Import (*.use) and select the files **WrongFile1.use – WrongFile4.use** contained in the Lesson2.zip archive.



Click on **Options** and, if the wrong sign convention is used in the data files, confirm that you want to change the sign of the imported current curve. After leaving the dialog box with **Import**, the current curves included in the imported files are shown on the screen.

20. Clicking on Document -> Add Simulations to RAM-Disk ( ) adds all simulated or experimental CVs involved in the active simulation document to an internal RAM-Disk managed by *DigiElch*. (Maybe the command should be named "Add Experimental CVs to RAM-Disk" but actually it makes no difference between a simulation and a experimental CV). Before moving the CVs to the RAM-Disk you will be asked whether you want to add an identification string to the file names (for a better distinction of the imported files). This is not necessary here. Let the input field empty and continue with **OK**.

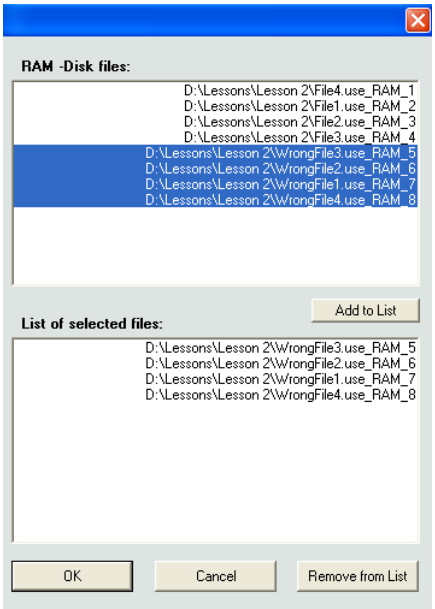
21. Click on Data Fitting->Prepare Fitting Project and complete the Chemical Reactions page in the following way:

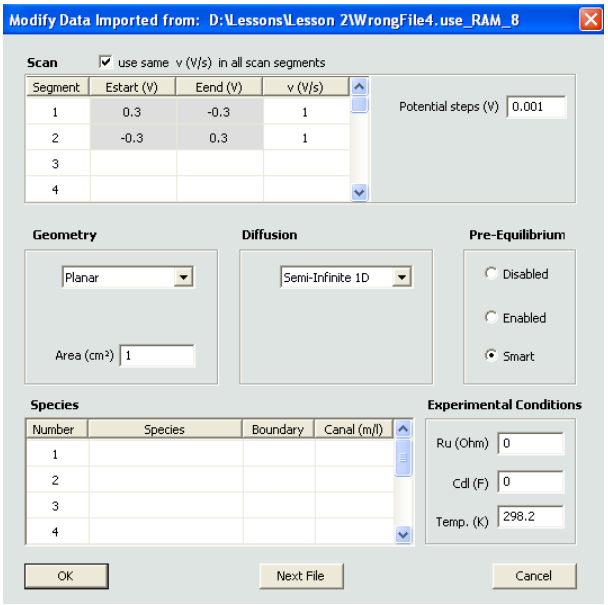


The input of mechanism and starting parameters as well as the selection of parameters optimized by the fitting procedure corresponds exactly to that in 10.-12. with the only difference that other species names ("Ox" and "Red" instead of "MyCompound" and "Something") were used and that a wrong analytical concentration has been entered for the oxidized form initially present when starting the experiment. This is done here for demonstrating that the latter does not matter provided the correct analytical concentration is assigned to each file imported by the fitting routine. This will be described in the following.

22. Click on Data Fitting->Select Target Curves form RAM-Disk ( ), select the four files **WrongFile1.use – WrongFile4.use** as shown below (left picture) and continue with **OK**.

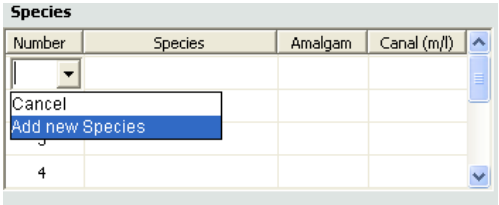
Then click on Data Fitting->Modify Selected Target Files. Since no template mechanism was entered in 19. most of the parameters shown in the appearing dialog box (right picture) refer to the default parameter setting and no species are shown





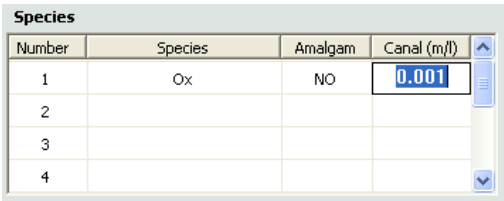
To get the correct assignment to the experimental parameters actually used in the underlying files it would be necessary now to enter not only the correct scan rate but also the correct **Geometry**, the correct **mass of the mercury drop** and the correct **analytical species concentrations**.

as



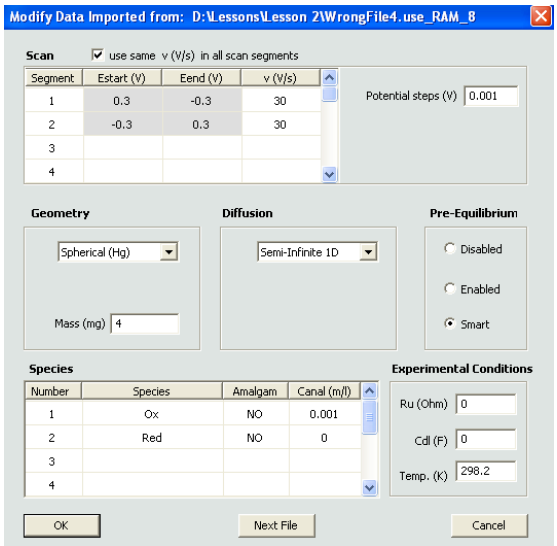
While scan rate, geometry and mercury mass are entered/selected usual we have to add the required species before defining their concentrations. This is accomplished by clicking on the index field associated with the first empty line in **Species** and selecting "Add new Species" as shown in the picture.

It is important here to emphasize that the species names must correspond to those used when defining the Mechanism & Starting Parameters in 21. Hence, enter "Ox" in the appearing dialog box and finish with **OK**.



Set the analytical concentration of "Ox" to *0.001* as shown in the picture. In the same way the species "Red" is added.

The dialog box referring to **WrongFile4.use** should look now as follows



Click on the **Next File** button and do the same modifications for the other files, too, and make sure that the correct scan rate is assigned to each file. (*1V/s* refers to **WrongFile1.use**, *3 V/s* to **WrongFile2.use**, *10 V/s* to **WrongFile3.use** and *30 V/s* to **WrongFile4.use**, respectively).

Now we have reached exactly the same situation as after completing 12 with the only difference that the same starting mechanism has been formulated with different species names. Consequently, continuing as described in 13-17 should yield identical results.

The user may have noticed that the correct assignment of the experimental parameters to the individual files becomes more and more tedious the greater the number of files and the more modifications must be done. Starting with a sensible template can save a lot of work.