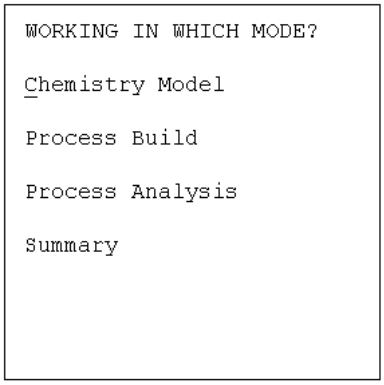
OLI Tips #36 Removing N2 from NOx oxidation and reduction.

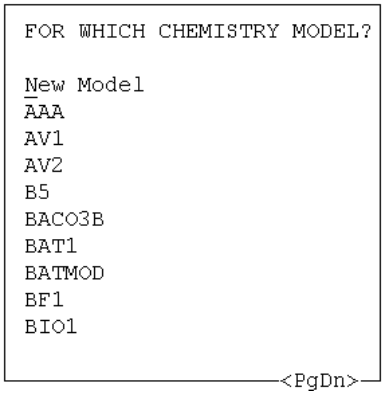
Revised February 2, 2010

The OLI oxidation and reduction chemistry involving nitrogen tends to create too much nitrogen gas (N_2). This is usually the most stable oxidation state for nitrogen but may require biological action (nitrogen fixation) to form. We will need to remove the N_2 forming equilibria from the generated model. To do this we need to use the chemistry model generator in either ESP or the Toolkit.

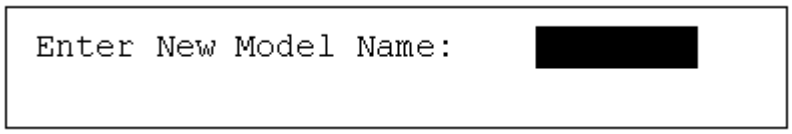
1. Start ESP or The toolkit.
2. Specify a process or stream name
3. This will display the initial screens for the chemistry model



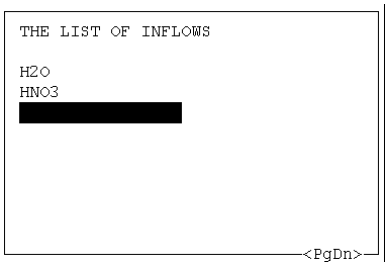
4. Select *Chemistry Model*.



5. Select a new model or an existing model. In this example we are selecting *New Model*

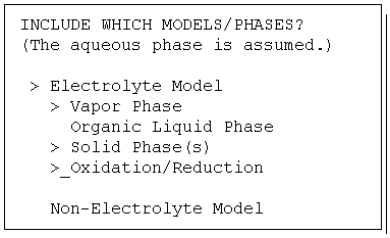


6. Enter the name of the model. In this example we are using “NOX2”

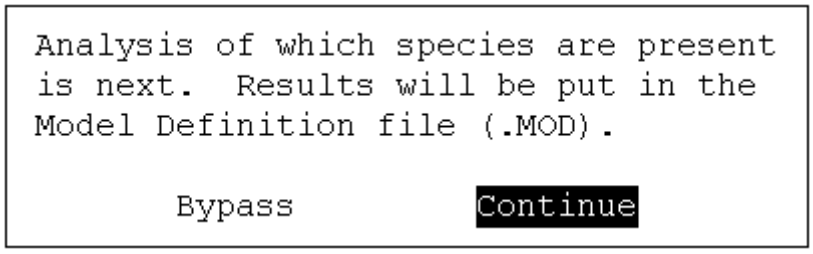


7. Enter your chemistry, make sure you have a source of nitrogen. In this case we are using HNO_3.

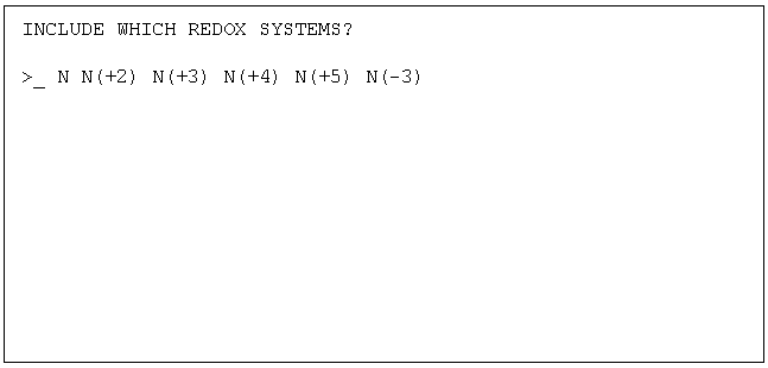
8. Press <Enter> on a blank line to continue.



9. Use the <Spacebar> to switch on the *Oxidation/Reduction* line. An “>” appears to indicate that has been switched on.
10. Press the <enter> key to continue.

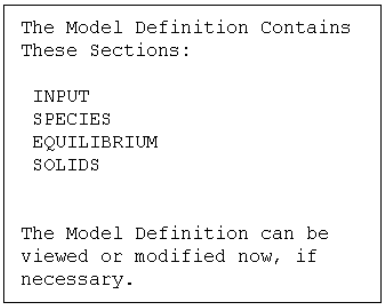


11. Select *Continue* to begin the model generation.

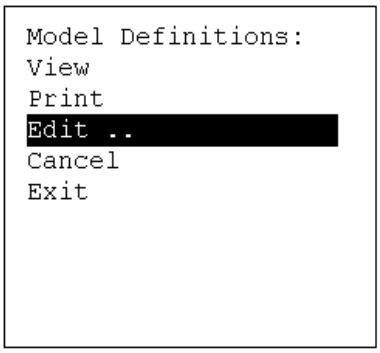


12. Use the <Spacebar> to select your redox subsystem. If you have more than one species in the model you may find many subsystems present. Select the nitrogen line, the ”>” indicates that the subsystem has been selected.

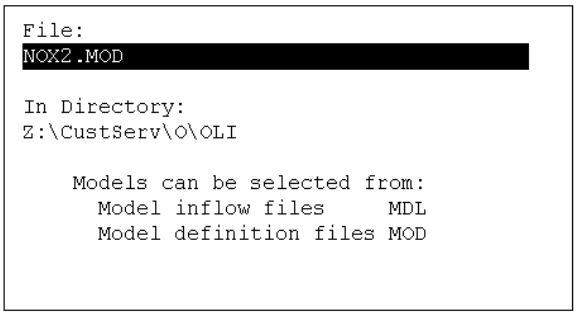
13. Press the <Enter> key to continue.
14. Press the <Enter> key when the screen stops scrolling.



15. The model has been partially completed. We now need to modify the model. Select <File> from the action line.

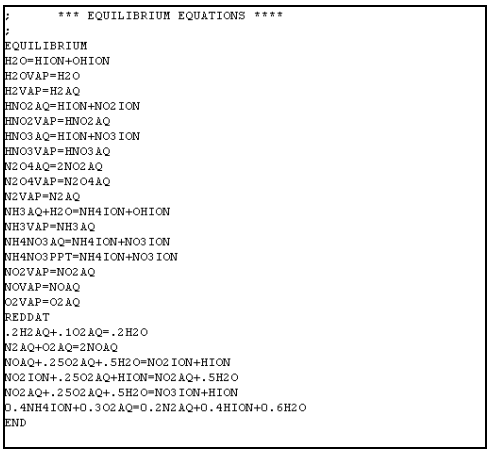


16. Select *Edit* from the list.



17. You may edit several files, we will edit the MOD file. Press <Enter> when done.

18. This will activate MS-Windows™ Notepad.EXE. The file may now be edited. Scroll down to the bottom of the window.



19. Locate the following equations at the bottom of this file:[1]

REDDAT
.2H2AQ+.1O2AQ=.2H2O
N2AQ+O2AQ=2NOAQ
NOAQ+.25O2AQ+.5H2O=NO2ION+HION
NO2ION+.25O2AQ+HION=NO2AQ+.5H2O
NO2AQ+.25O2AQ+.5H2O=NO3ION+HION
0.4NH4ION+0.3O2AQ=0.2N2AQ+0.4HION+0.6H2O

This is the oxidation reduction section of the chemistry model. There are two pathways to forming N_2. These are:

N2AQ+O2AQ=2NOAQ

and

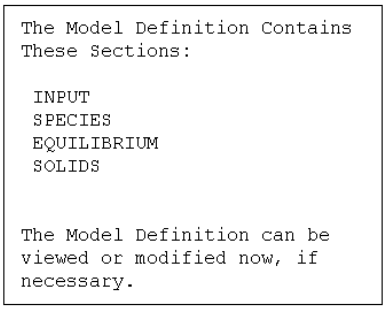
[1] For MSE the chemistry has changed. See the appendix for the new chemistry.

0.4NH4ION+0.3O2AQ=0.2N2AQ+0.4HION+0.6H2O

These must be removed from the model. The easiest method to remove them is to add a semi-colon ";" in front of each equilibrium. The revised section should now look like this:

REDDAT
.2H2AQ+.1O2AQ=.2H2O
;N2AQ+O2AQ=2NOAQ
NOAQ+.25O2AQ+.5H2O=NO2ION+HION
NO2ION+.25O2AQ+HION=NO2AQ+.5H2O
NO2AQ+.25O2AQ+.5H2O=NO3ION+HION
;0.4NH4ION+0.3O2AQ=0.2N2AQ+0.4HION+0.6H2O

20. Use File and Save to save this file. You should be returned to this screen.



21. Press the <Enter> key and continue generating the model. The pathway to forming Nitrogen gas from other nitrogen species has been removed. You can still use nitrogen as an inert gas.

Appendix: Changes for MSE

The mixed-solvent electrolyte chemistry differs slightly from the traditional AQ framework in that we have added several new species. The species hydroxylamine[2] and hydrazine[3] have been added.

This creates a new pathway to nitrogen that differs from the AQ framework. Here is the complete REDOX[4] section of the model:

```
REDDAT
N2AQ+1.5OHION+1.5H3OION=2HDROXAMNAQ+0.5O2AQ
NOAQ+0.75OHION+0.75H3OION=HDROXAMNAQ+0.75O2AQ
NO2ION+H3OION=HDROXAMNAQ+O2AQ
NO2AQ+0.75OHION+0.75H3OION=HDROXAMNAQ+1.25O2AQ
NO3ION+H3OION=HDROXAMNAQ+1.5O2AQ
NH4ION+0.5O2AQ+0.5OHION=HDROXAMNAQ+0.5H3OION
N2OAQ+1.5OHION+1.5H3OION=2HDROXAMNAQ+O2AQ
N2H4AQ+0.5O2AQ+0.5OHION+0.5H3OION=2HDROXAMNAQ
.2H2AQ+.1O2AQ=.2H2O
```

The pathway to nitrogen is:

```
N2AQ+1.5OHION+1.5H3OION=2HDROXAMNAQ+0.5O2AQ
```

And is the only equation that has to be eliminated. Put a semi-colon in front of the equation and complete the steps as indicated above.

```
;N2AQ+1.5OHION+1.5H3OION=2HDROXAMNAQ+0.5O2AQ
```

[2] ESP Name HYDROXAMN
[3] ESP Name N2H4
[4] Based on ESP version 8.2.1 or later