



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

Revised February 2, 2010

The OLI oxidation and reduction chemistry involving nitrogen tends to create too much nitrogen gas (N₂). 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 N₂ 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

```
WORKING IN WHICH MODE?  
  
Chemistry Model  
  
Process Build  
  
Process Analysis  
  
Summary
```

4. Select *Chemistry Model*.

```
FOR WHICH CHEMISTRY MODEL?  
  
New Model  
AAA  
AV1  
AV2  
B5  
BACO3B  
BAT1  
BATMOD  
BF1  
BIO1  
  
-<PgDn>-
```

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

Enter New Model Name:

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

```
THE LIST OF INFLOWS
H2O
HNO3

<PgDn>
```

7. Enter your chemistry, make sure you have a source of nitrogen. In this case we are using HNO₃.
8. Press <Enter> on a blank line to continue.

```
INCLUDE WHICH MODELS/PHASES?
(The aqueous phase is assumed.)

> Electrolyte Model
> Vapor Phase
  Organic Liquid Phase
> Solid Phase(s)
> _ Oxidation/Reduction

Non-Electrolyte Model
```

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.

```
Analysis of which species are present
is next. Results will be put in the
Model Definition file (.MOD).
```

Bypass

Continue

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

```
INCLUDE WHICH REDOX SYSTEMS?  
  
>_ N N(+2) N(+3) N(+4) N(+5) N(-3)
```

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.

```
The Model Definition Contains  
These Sections:  
  
INPUT  
SPECIES  
EQUILIBRIUM  
SOLIDS  
  
The Model Definition can be  
viewed or modified now, if  
necessary.
```

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

```
Model Definitions:  
View  
Print  
Edit ..  
Cancel  
Exit
```

16. Select *Edit* from the list.

```

File:
NOX2.MOD

In Directory:
Z:\CustServ\O\OLI

Models can be selected from:
Model inflow files MDL
Model definition files MOD

```

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

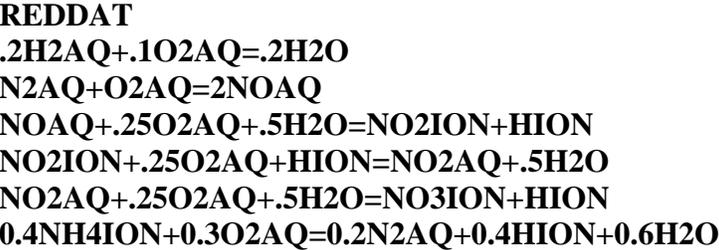
18. This will activate MS-Windows™ Notepad.EXE. The file may now be edited. Scroll down to the bottom of the window.

```

*** EQUILIBRIUM EQUATIONS ****
/
EQUILIBRIUM
H2O=HION+OHION
H2OVAP=H2O
H2VAP=H2AQ
HN02AQ=HION+NO2ION
HN02VAP=HN02AQ
HN03AQ=HION+NO3ION
HN03VAP=HN03AQ
N2O4AQ=2NO2AQ
N2O4VAP=N2O4AQ
N2VAP=N2AQ
NH3AQ+H2O=NH4ION+OHION
NH3VAP=NH3AQ
NH4NO3AQ=NH4ION+NO3ION
NH4NO3PPT=NH4ION+NO3ION
NO2VAP=NO2AQ
NO3VAP=NO3AQ
O2VAP=O2AQ
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
END

```

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



This is the oxidation reduction section of the chemistry model. There are two pathways to forming N₂. These are:



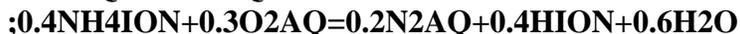
and

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



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



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

```
The Model Definition Contains
These Sections:

INPUT
SPECIES
EQUILIBRIUM
SOLIDS

The Model Definition can be
viewed or modified now, if
necessary.
```

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 hydroxylamine² and hydrazine³ have been added.

This creates a new pathway to nitrogen that differs from the AQ framework. Here is the complete REDOX⁴ 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
N2O AQ+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