Homework #10 Solution

The biggest issue with this homework is trying to figure out what conditions to run. It’s not entirely clear from the text of the paper. But looking at the initial conditions (at around 10^{-7} s), it’s clear this is CO/H_2/N_2/O_2, not CH_4/air. So you have to start with those species. What ratio? Again, that’s not so clear, but extracting data from the plot at the earliest time shows only reactants above mole fractions of about 10^{-5}, so this should be a great estimate. I get something like N_2:0.639, CO:0.074, H_2:0.185, O_2:0.102, which, when I put into GASEQ to get AFT gives about the right temperature of 2477 K for 10 atm and 1000 K input. A second look this year suggests maybe CO is closer to 0.08, but it’s a negligible difference.

Once you get around to running that with GRI, you see that ignition times are much, much longer, of the order of 10^{-3} to 10^{-2} s, as opposed to 10^{-5} s. Still, you need to look at dynamics relative to the appearance of the flame (i.e. on the order of 10^{-5} s near the flame) to resolve key kinetics. So I set the flame sheet to t = 10^{-5} s and reset the times to get the attached plots.

In addition to the delayed ignition, the following points should be noted:

1) NO rises on a very similar time scale from the appearance of the flame, producing very close to the same amount of NO as Marteney predicted at 10^{-2} s.
2) Some NO is produced in the flame sheet – more than Marteney predicts, but most still follows the delayed route.
3) N is much less than predicted by Marteney
4) There’s a problem with water vapor. There’s not enough hydrogen in the final products for an elemental balance if you use the lines given. The major discrepancy is H_2O. Everything else matches well. So the H_2O line is almost certainly incorrect in the original plot and that recreated for the text.
5) The temporal width of the flame zone is similar, but slightly shorter than Marteney predicts.

In general, the simulations (with the exception of the delay time), agree surprisingly well with modern mechanisms, especially considering the level of reduced mechanism used by Marteney.

The mistaken H_2O line is somewhat of concern, but, in my opinion, represents more the state of science and peer review than anything. Dig deep enough into ANY paper, and I’d suspect you find some errors. Science is done by humans. Peer review didn’t catch this, though it could have with a quick elemental balance check. I’d suspect very few reviewers would go into that much detail. This particular error doesn’t substantively affect the results, but it’s significant. I chose this one replication at random, and it had an error. How many other plots in this paper and others have similar problems. Key point: Just because a study makes it to print in a good journal and has passed rigorous peer review, doesn’t mean it’s right. Independent replication of a result remains the gold standard, and that’s almost never done.
Adiabatic, constant P, 0-D, 1000 K initial temperature \(N_2/CO/H_2/O_2 = 0.639/0.074/0.185/0.102\). GRI 3.0

Mole Fraction

Time (s) - Ref'd to flame = 1e-5
If we just take the derivative of the [NO] data, we get a choppy curve shown below, showing a peak in the flame zone, then a long tail. I’ve added the full d[NO]/dt from a more complete analysis (see below), and they agree pretty well.

Considering the 8 reactions we chose:

1. N2+OH → NH+NO
2. N2+O → N+NO
3. NNH+O → NH+NO
4. N+O2→ NO+O
5. C+N2 → CN+N
6. CH+N2 → HCN+N
7. CH2+N2 → HCN+NH
8. CH2(S)+N2 → NH+HCN

The first two reactions are the thermal mechanism N2 breaking reactions. Reaction 3 is the main NO producing reaction in the NNH mechanism. Reaction 4 is the reaction of free N with O2 as part of the thermal mechanism. The last 4 reactions are the N2 breaking reactions in the prompt mechanism.

Let’s just look at these first without going into too much depth:
Even considering the ‘quick-look’ approach, we can get a lot of information from this analysis. First off, the “Prompt” reactions are much smaller than thermal or NNH mechanism. Since this is syngas combustion, that’s not surprising. There’s not a lot of the C, CH, CH₂ radicals around in these flames, so we’d expect prompt contributions to be small. If the fuel were CH₄, I’d expect a much bigger contribution.

Second, by comparing the NNH and thermal routes, it looks like NNH is more active early (as expected b/c it’s more like a prompt mechanism), but it still persists late. The thermal route seems to dominate over time (remember both scales are log scales, so the difference is actually pretty big). But to some extent we’re comparing apples and orange b/c in one case we’re measuring N₂ breaking, and in the other, we’re measuring NO formation from NNH. Neither tells the complete story. Plus, there are other reactions of importance in each mechanism, especially the NNH.

To take a ‘deep dive’ approach, we’d need to look at all reactions involving NO and N₂ (the source of all NO). We’d need to look at backwards reactions as well, not just forward reactions. And we’d need to differentiate NO formation from N₂ breaking, though they’re clearly linked.

Let’s go ahead and do that. We’ll start with reactions involving NO. Here’s the list:

1. N+NO→N₂+O 2.700E+13 0.000 355.00
2. N+O₂→NO+O 9.000E+09 1.000 6500.00
3. N+OH→NO+H 3.360E+13 0.000 385.00
4. N₂O→N₂+NO 2.900E+13 0.000 23150.00
5. NO₂+NO→N₂O₂+OH 2.110E+12 0.000 -480.00
6. NO+M→N₂+M 1.060E+20 -1.410 0.00
  H₂/2.00/ H₂O/6.00/ CH₄/2.00/ CO/1.50/ CO₂/2.00/ C₂H₆/3.00/ AR/ .70/
7. NO₂→NO+O 3.900E+12 0.000 -240.00
8. NO+H→NO+H₂O 1.320E+14 0.000 360.00
9. NH+O→N₂+OH 4.000E+13 0.000 0.00
10. NH₂+O→NO+OH 1.280E+06 1.000 100.00
11. NH+O₂→NO+OH 2.160E+13 -0.230 0.00
12. NH+NO→N₂+OH 3.650E+14 -0.450 0.00
13. NNH+O→NO+OH 7.000E+13 0.000 0.00
14. HNO+O→NO+OH 2.500E+13 0.000 0.00
15. HNO+H→H₂+NO 9.000E+11 0.720 660.00
16. HNO+OH→NO+H₂O 1.300E+07 1.900 -950.00
17. HNO+O₂→HO₂+NO 1.000E+13 0.000 13000.00
18. NCO+O→N₂+OH 2.350E+13 0.000 0.00
19. NCO+OH→NO+H₂O 0.250E+13 0.000 0.00
20. NCO+O₂→NO+CO₂ 2.000E+12 0.000 20000.00
21. NCO+NO→N₂+CO₂ 1.900E+17 -1.520 740.00
22. NCO+NO→N₂+CO₂ 3.800E+18 -2.000 800.00
23. C+NO→CN+O 1.900E+13 0.000 0.00
24. C+NO→CO+N 2.900E+13 0.000 0.00
25. CH+NO→HCN+O 4.100E+13 0.000 0.00
26. CH+NO→H+CNO 1.620E+13 0.000 0.00
27. CH+NO→N+HCO 2.460E+13 0.000 0.00
28. CH₂+NO→H₂+HCNO 3.100E+17 -1.380 1270.00
29. CH₂+NO→OH+HCN 2.900E+14 -0.600 760.00
30. CH₂+NO→H₂+HCNO 3.800E+13 -3.600 580.00
31. CH₂+NO→H₂+HCNO 3.100E+17 -1.380 1270.00
32. CH₂+NO→OH+HCN 2.900E+14 -0.690 760.00
33. CH₂+NO→H₂+HCNO 3.800E+13 -3.600 580.00
34. CH₃+NO→H₂+HCNO 9.600E+13 0.000 288000.00
35. CH₃+NO→H₂+HCNO 1.000E+12 0.000 21750.00
36. HCN+O→H₂+HCNO 2.000E+12 0.000 0.00
37. HCCO+NO→HCN+CO 0.900E+13 0.000 0.00
38. CN+NO₂→CNO+NO 6.160E+15 -0.752 345.00
39. N+CO₂→NO+CO 3.000E+12 0.000 11300.00
That’s a lot of reactions! But I’ll grind through them, and let’s see what we get. I took all 39 reactions and calculated forward and backwards reaction progress to get a net Rate of Progress, where + is net forward production, and – is net backward. I did one simplification, and that was that for reaction 6, I just multiplied the rate by 1.5x instead of doing the rate for each species. It’s a fair approximation.

This plot shows the 13 most active reactions with respect to production of NO. I’ve focused on the direction of reaction that produces NO, so some of the curves represent a net forward rate and some a net backward rate. If the destruction rate exceeds the production rate (e.g. grey and yellow curves), then that part of the curve is not shown. Also, I’ve had to cut a few reactions off after about 1.5e-4 s due to numerical noise. On the next page, I zoom in a bit on this plot to highlight the central region where all the action is occurring.
Postive [NO] Production Rate $\text{mol/cm}^3/\text{s}$

$\text{N}+\text{NO}\leftrightarrow\text{N}_2+\text{O}$

$\text{N}+\text{O}_2\leftrightarrow\text{NO}+\text{O}$

$\text{N}+\text{OH}\leftrightarrow\text{NO}+\text{H}$

$\text{NO}+\text{O}+\text{M}\leftrightarrow\text{NO}_2+\text{M}$

$\text{NO}_2+\text{O}\leftrightarrow\text{NO}+\text{O}_2$

$\text{NO}_2+\text{H}\leftrightarrow\text{NO}+\text{OH}$

$\text{NH}+\text{O}\leftrightarrow\text{NO}+\text{H}$

$\text{NH}+\text{NO}\leftrightarrow\text{N}_2+\text{OH}$

$\text{NH}+\text{NO}\leftrightarrow\text{N}_2\text{O}+\text{H}$

$\text{NH}+\text{O}\leftrightarrow\text{NH}+\text{NO}$

$\text{HNO}+\text{O}\leftrightarrow\text{NO}+\text{OH}$

$\text{HNO}+\text{H}\leftrightarrow\text{H}_2+\text{NO}$

$\text{HNO}+\text{OH}\leftrightarrow\text{NO}+\text{H}_2\text{O}$

$\text{N}+\text{CO}_2\leftrightarrow\text{NO}+\text{CO}$
The reactions producing the most NO are not necessarily the ones I’d expect, but you can definitely see thermal routes ($N_2 + O$, $N + O_2$, $N+OH$), as well as NNH routes (NNH+O, reactions of NH), and the $N_2O$ route ($N_2O + H$). Prompt reactions are strong in the flame zone, while delayed reactions are relatively strong in the late time. Since it’s a log scale on the x-axis, late time results weigh more heavily in terms of overall production. If we time integrate these curves to get total production, I get the following:

<table>
<thead>
<tr>
<th>Total NO</th>
<th>Reaction</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.02275E-08</td>
<td>HNO+OH$\leftrightarrow$NO+H2O</td>
<td>NNH</td>
</tr>
<tr>
<td>5.11161E-09</td>
<td>N+NO$\leftrightarrow$N2+O</td>
<td>Thermal</td>
</tr>
<tr>
<td>3.56945E-09</td>
<td>NO+O+M$\leftrightarrow$NO2+M</td>
<td>All mechanisms</td>
</tr>
<tr>
<td>3.54146E-09</td>
<td>N+OH$\leftrightarrow$NO+H</td>
<td>Thermal</td>
</tr>
<tr>
<td>2.29335E-09</td>
<td>HNO+H$\leftrightarrow$H2+NO</td>
<td>NNH</td>
</tr>
<tr>
<td>1.81379E-09</td>
<td>NNH+O$\leftrightarrow$NH+NO</td>
<td>NNH</td>
</tr>
<tr>
<td>1.41927E-09</td>
<td>NH+NO$\leftrightarrow$N2O+H</td>
<td>NO2</td>
</tr>
<tr>
<td>7.18356E-10</td>
<td>N+CO2$\leftrightarrow$NO+CO</td>
<td>Thermal</td>
</tr>
<tr>
<td>5.22519E-10</td>
<td>NO2+H$\leftrightarrow$NO+OH</td>
<td>NO2</td>
</tr>
<tr>
<td>4.96833E-10</td>
<td>NH+NO$\leftrightarrow$N2+OH</td>
<td>Thermal</td>
</tr>
<tr>
<td>2.41021E-10</td>
<td>NH+O$\leftrightarrow$NO+H</td>
<td>NNH</td>
</tr>
<tr>
<td>1.95783E-10</td>
<td>N+O2$\leftrightarrow$NO+O</td>
<td>Thermal</td>
</tr>
<tr>
<td>4.42564E-11</td>
<td>HNO+O$\leftrightarrow$NO+OH</td>
<td>NNH</td>
</tr>
</tbody>
</table>

I’ve made the mechanism assignments based on some assumptions, mostly that NH primarily comes from NNH, which means that HNO, which comes primarily from NH, is indicative of the NNH mechanism. Some NH comes from reactions like $N_2+OH \rightarrow NH + NO$, so this overestimates NNH mechanism effect. Also, I’m associating N with the thermal mechanism, though some is likely produced in other mechanisms as well. There’s an equilibrium between NO2 and NO that is shown in the third reaction – whenever you get NO or NO2, you also get the other.

This analysis suggests that the primary NO formation mechanism is NNH here, with strong contributions from thermal, and non-negligible N2O contributions. But negligible prompt (hydrocarbon fragment $N_2$ breaking) contribution. Again, not entirely unexpected since this is syngas, with a lot of $H_2$ around, and pretty high temperatures.

Let’s now look at $N_2$ breaking reactions. Remember that all the NO comes originally from $N_2$, so seeing what reactions break up $N_2$ gives great insight into NO formation. Though not all broken $N_2$ goes to NO. I picked all the reactions with $N_2$ in them, then cut out a few to make my life simpler (those involving HCNN and $CH_4$). Not sure how much that affects things. I also used high pressure limit for the pressure dependent reactions, and 1.5x on reactions with multiple $3^{rd}$ body efficiencies. I should still be in the ballpark on these estimates, though the numbers will be less accurate.
Here’s my reaction list:

1. \(N+N_{2} \leftrightarrow N_{2}+O\)  
2. \(N_{2}O+O \leftrightarrow N_{2}+O_{2}\)  
3. \(N_{2}O+H \leftrightarrow N_{2}+OH\)  
4. \(N_{2}O+OH \leftrightarrow N_{2}+H_{2}O\)  
5. \(N_{2}O \leftrightarrow N_{2}+O\)  
6. \(NH+N \leftrightarrow N_{2}+H\)  
7. \(NH+NO \leftrightarrow N_{2}+OH\)  
8. \(NNH \leftrightarrow N_{2}+H\)  
9. \(NNH+M \leftrightarrow N_{2}+H+M\)  
10. \(NNH+O \leftrightarrow O_{2}+N_{2}\)  
11. \(NNH+OH \leftrightarrow H_{2}O+N_{2}\)  
12. \(NCO+N \leftrightarrow N_{2}+CO\)  
13. \(C+H_{2} \leftrightarrow CN+N\)  
14. \(CH\)  
15. \(CH_{2} \leftrightarrow CH_{3}\)  
16. \(NH\)  
17. \(CH_{2}\)  
18. \(CH_{2}+N_{2} \leftrightarrow HCN+NH\)  
19. \(CH_{2}S+N_{2} \leftrightarrow NH+HCN\)  

On the next pages is the plot of \(N_{2}\) destruction rate for the 9 most active \(N_{2}\) breakers. The plot is a bit ugly late b/c some reactions (esp. those with NNH and \(N_{2}\)) become very sensitive to the difference between two large numbers. Since the mole fractions in the output file are given to only 3 significant figures, the analysis gets noisy. Nevertheless, you can see some key trends. In the flame zone, the two NNH reactions are the primary \(N_{2}\) breakers, with the \(N_{2}O\) formation a close third. Nothing else is significant.

Later in the flame, the NNH and \(N_{2}O\) mechanisms continue to be important, but the thermal mode (red, blue, pync) curves start to contribute more significantly.

Again, there’s no evidence for prompt mechanisms.

Summary:
A more detailed analysis of NO formation looks at all reactions involving NO and \(N_{2}\) (from which NO evolves). Forward and backward rates need to be considered. Integrated effect is important, not just peak production rate.

Looking at all of this shows that three mechanisms are important here NNH, thermal, and \(N_{2}O\), while the prompt mechanism is not significant. The NNH mechanism produces the most NO, probably followed by thermal, then \(N_{2}O\) mechanisms.
$[N_2]$ Destruction Rate $\text{mol/cm}^3/s$

- $NNH+M \leftrightarrow N_2+H+M$
- $N+NO \leftrightarrow N_2+O$
- $N_2O(+M) \leftrightarrow N_2+O(+M)$
- $NNH \leftrightarrow N_2+H$
- $N_2O+H \leftrightarrow N_2+OH$
- $NH+NO \leftrightarrow N_2+OH$
- $NNH+OH \leftrightarrow H_2O+N_2$
- $NNH+H \leftrightarrow H_2+N_2$
- $N_2O+OH \leftrightarrow N_2+HO_2$