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Reduced Equations for Calculating the Combustion Rates of Jet-A and Methane Fuel

Melissa Molnar
Ohio University, Athens, Ohio

C. John Marek
Glenn Research Center, Cleveland, Ohio

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Melissa Molnar
Ohio University
Athens, Ohio 45701

C. John Marek
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

ABSTRACT

Simplified kinetic schemes for Jet-A and methane fuels were developed to be used in numerical combustion codes, such as the National Combustor Code (NCC) that is being developed at Glenn. These kinetic schemes presented here result in a correlation that gives the chemical kinetic time as a function of initial overall cell fuel/air ratio, pressure and temperature. The correlations would then be used with the turbulent mixing times to determine the limiting properties and progress of the reaction.

A similar correlation was also developed using data from the NASA's Chemical Equilibrium Applications (CEA) code to determine the equilibrium concentration of carbon monoxide as a function of fuel air ratio, pressure and temperature.

The NASA Glenn GLSENS kinetics code calculates the reaction rates and rate constants for each species in a kinetic scheme for finite kinetic rates. These reaction rates and the values obtained from the equilibrium correlations were then used to calculate the necessary chemical kinetic times. Chemical kinetic time equations for fuel, carbon monoxide and NO_x were obtained for both Jet-A fuel and methane.

Introduction

Reaction rates are kinetically limited at low temperatures and mixing limited at very high temperatures. According to the Magnussen model (reference 1), the fuel oxidation rate will be determined by the maximum of either the kinetic time or the turbulent mixing times of the fuel and air. However, for large numerical solutions it is very tedious to use complete classical calculations to compare both the kinetic and turbulent mixing times to determine the region of the reaction. Conventional chemical kinetic schemes are extremely time consuming for two and three dimensional computer calculations for combustors. Large mechanisms with many intermediate species and very fast radical reactions cause the equations to be stiff (extremely fast compared to the overall rate, requiring a large number of small time steps), making them very difficult to integrate. Calculations for these extensive mechanisms are repetitive and complex. Using the simplified kinetic scheme developed here to calculate the three chemical kinetic times greatly reduces the amount of time required to compare kinetic reaction times with turbulent mixing times and will reduce the time required to obtain a converged solution. The advantage of computing the chemical kinetic time for only the species of interest is

that we have only the differential equations of interest to solve, resulting in a much smaller set of equations.

This method is for use in Computational Fluid Dynamics (CFD) calculations where chemical kinetics is important. The current version of NCC requires the user to decide to use either chemical kinetics or the turbulent mixing rates. Following conventional methods would not allow for the calculation of both in a reasonable amount of time. The derived method allows for a quick and easy comparison over the complete spectrum of conditions. This scheme is intended for use in numerical combustion codes, but it can also be used as a quick and accurate method to calculate chemical reaction rates.

We have also curve fitted the equilibrium concentrations of CO, O_2, and NO_x using data generated by the NASA Chemical Equilibrium Application code (CEA). The CO equilibrium correlation was then used in the calculation of the chemical kinetic time. Although this research focused on Jet-A Fuel and methane, this method may be used for any system. Jet-A fuel was represented as $C_{12}H_{23}$, using Krishna Kundu's twenty three step mechanism (reference 2 and 3). GLSENS (reference 4) was used to integrate the system of equations, at over 400 conditions to derive the rate expressions. It may be reasoned that the presented equations are only as good as the overall mechanism that calculates the data. However, performing the calculations in the conventional manner is also only as good as the mechanism equations and constants that go into them.

Simple Time Model

The simple model derived here is to be used with the Magnussen mixing model of combustion (reference 1). The turbulent mixing time is shown as a function of the reaction's turbulent kinetic energy and dissipation rate.

$$\text{Net rate} \quad \varpi_r = min(\frac{A\varepsilon}{k} y_{fuel}, \frac{A\varepsilon}{k}\frac{y_{oxygen}}{r_f}, \varpi_{kinetic}) \tag{1}$$

Where $\frac{k}{A\varepsilon}$ equals the turbulent mixing time, τ_m. The mixing constant, A, is usually given as 4.0. The factor $\frac{y_{fuel}}{\varpi_{kinetic}}$ is the chemical kinetic time τ_c.

In order to obtain the chemical source term ϖ_r, a comparison is made of the mixing rate, $\frac{1}{\tau_m}$ and the chemical kinetic rate $\frac{1}{\tau_c}$, and the lowest rate or the longest time is used in the expression; see Figure 1. This may also be represented by the following relationship:

$$\tau = \max(\tau_m, \tau_c) \tag{2}$$

Model Equations

The following equations can be used to model the chemical system.

$$Fuel + O_2 \xrightarrow{\tau_{Fuel}} CO + H_2O \quad \text{(S1)}$$

$$CO + \frac{1}{2}O_2 \xrightarrow{\tau_{CO}} CO_2 \quad \text{(S2)}$$

$$N_2 + O_2 \xrightarrow{2\ \tau_{NO}} 2NO \quad \text{(S3)}$$

The following first order reaction was used to represent the rate of fuel burning. (In this report, t and τ are given in milliseconds, while concentrations are given in gmoles/cc):

$$\frac{dFuel}{dt} = -\frac{Fuel}{\tau_{Fuel}} \quad (3)$$

The fuel concentration is then represented by a simple exponential decay expression, where F_0 is the initial fuel concentration.

$$Fuel = F_o e^{\left(\frac{-t}{\tau_{Fuel}}\right)} \quad (4)$$

The carbon monoxide reaction rate was represented by Equations (5) and (5a). The fuel concentration is multiplied by a factor of 12 because the Jet-A fuel takes the formula $C_{12}H_{23}$. Equation (5b) is the solution to the differential equation showing the CO concentration as a function of initial fuel concentration, CO equilibrium concentration and the chemical kinetic times.

$$\frac{dCO}{d\tau} = -\frac{(CO - COeq)}{\tau_{CO}} + \frac{12Fuel}{\tau_{Fuel}} \quad (5)$$

and

$$\frac{dCO_2}{dt} = \frac{CO}{\tau_{CO}} \quad (5a)$$

$$CO - CO_{eq} = e^{\frac{-t}{\tau_{CO}}} (CO(t=0) - CO_{eq} - \frac{12F_o\tau_{CO}}{\tau_f - \tau_{CO}}) + \frac{12F_o\tau_{CO}}{\tau_f - \tau_{CO}} e^{-\frac{t}{\tau_f}} \qquad (5b)$$

Since *CO* is an intermediate species going towards equilibrium, it is difficult to precisely determine its chemical kinetic time. At long times if *CO* equilibrium differs from the system equilibrium large errors are generated as *dCO*/*dt* goes to zero or:

$$\tau_{CO} = \frac{CO - CO_e}{dCO/dt} \Rightarrow \frac{error}{0}.$$

A more robust procedure was to use equation (5a). Then

$$\tau_{CO} = \frac{CO}{dCO_2/dt}.$$

This expression was used for CH_4, because $Co_e >> CO$. However, the use of CO_e and τ_{CO} in NCC calculations with equation (5) and (5b) should provide the correct limits for *CO* in the calculation.

Finally, the nitrogen oxide formation rate, a species important for combustor emissions, was modeled as a simple zero order expression.

$$\frac{dNO_x}{dt} = \frac{1}{\tau_{NO_x}} \qquad \text{or} \qquad NO_x = \frac{t}{\tau_{NO_x}} \qquad (6)$$

Equilibrium Correlations

A correlation was needed to represent the *CO* equilibrium concentration as a function of overall cell fuel/air ratio, pressure and temperature. Equilibrium data was generated using the NASA Chemical Equilibrium Applications (CEA) program of reference 5. A total of three hundred cases were computed and then correlated using Excel. The following three possible correlations were tested. Table 1 shows the similarity between coefficients *b* and *c* for the three equations.

$$CO_{eq} = A(f/a)^b P^c exp[d/T] \qquad (7)$$

$$CO_{eq} = A(f/a)^b P^c exp[dT] \qquad (8)$$

$$CO_{eq} = A(f/a)^b P^c T^d \qquad (9)$$

Table 1. Comparison of Equilibrium Coefficients from Three Correlations

	A	b	c	d
Equation 7	4.43	1.69	0.513	-31840
Equation 8	1.37e-15	1.71	0.475	9.54e-3
Equation 9	2.13e-69	1.27	0.492	18.7

Multiple linear regression in a Microsoft Excel spreadsheet was used to determine the coefficients A, b, c, and d for each equation. (A detailed procedure on multiple linear regression can be found in Appendix A). Values for the equilibrium CO concentration were then calculated at each set of conditions using the above correlations and compared to the experimental values. All three equations produced similar results with a high correlation coefficient greater than 0.995, as seen in Figure 2. Equation 7 was chosen in this report for all temperature relations because of its similarity to the activation energy relation, $e^{-\frac{E}{RT}}$. Comparing this to the exponential term of equation 7 results in the approximation of coefficient *d* as *E*/*R*.

This temperature function was used for all correlations in this report. The entire Jet-A CEA data set was initially regressed and a parity plot showing the difference between experimental and calculated values was generated. However, the data behaved differently after reaching an equivalence ratio of one. Therefore the data was split into a lean group (fuel air ratio < 0.068) and a rich group (fuel air ratio ≥ 0.068) and regressed again, resulting in two separate correlations. Figures 3 and 4 are parity plots of the *CO* equilibrium correlations that show the similarity of the experimental and predicted values. The x-axis contains equilibrium values from CEA and the y-axis contains values calculated at the same set of conditions using the equilibrium correlations. Figure 4 showed more scatter at stoichiometric equivalence ratios than the lean side.
The same procedure was used to develop correlations for the equilibrium values of oxygen and NO_x. The *CO* equilibrium correlations for both Jet-A fuel and methane may be found in Table 2. The NO_x and oxygen equilibrium correlations may be found in Appendix B. Table 2 shows the similarity between the coefficients of Jet-A and methane for both the lean and rich cases.

Table 2. Carbon Monoxide Equilibrium Correlations

	Lean **f/a < 0.068**	**Rich** **f/a ≥ 0.068**
Jet-A Fuel	$CO_{eq} = 4.43\left(\frac{f}{a}\right)^{1.69} P^{0.513}\left[\exp(\frac{-31840}{T})\right]$	$CO_{eq} = 5.85e^{-3}\left(\frac{f}{a}\right)^{3.82} P^{0.961}\left[\exp(\frac{-969}{T})\right]$
	f/a < 0.059	**f/a ≥ 0.059**
Methane	$CO_{eq} = 4.98\left(f/a\right)^{1.74} P^{0.512}\left[\exp(\frac{-31797}{T})\right]$	$CO_{eq} = 1.11e^{-2}\left(f/a\right)^{3.90} P^{0.964}\left[\exp(\frac{-1235}{T})\right]$

Determination of the Chemical Kinetic Time

With the approach derived here, a simple direct comparison can be made between the mixing and chemical kinetic times and the minimum rate used for the computation as shown in Figure 1. The integration was performed for 400 cases shown below for Jet-A and methane fuels.

Pressure 1 to 40 atmospheres	(increments of 10 atmospheres)
Temperature 1000 to 2500K	(increments of 500K)
Equivalence ratios 0.3 to 1.0	(increments of 0.1)
1.0 to 2.0	(increments of 0.1)

Calculations were performed isothermally using GLSENS for each condition over a time of 0 to 10 milliseconds. By computing the progress isothermally, the chemical rate constants were fixed and the chemical kinetic time was determined as a unique value of temperature, pressure and initial fuel/air ratio. GLSENS computes the cumulative rate of reaction for each species from all equations in the mechanism, so it is a simple matter to then compute the chemical kinetic time for each species. For the fuel equation (3) the chemical kinetic time is given as

$$\tau_f = -\frac{Fuel}{\left(\frac{dFuel}{dt}\right)} \tag{10}$$

This simple calculation was done using additional steps in the GLSENS code (see Appendix E). Values for the chemical kinetic time were calculated for each concentration at each output time and each set of conditions. The trapezoidal rule (using $1/\tau$) was then used to calculate the best value of the chemical kinetic time for each set of conditions and the final numbers regressed over the complete set of cases to obtain the final correlation. The fuel, *CO*, and NO_x correlations are of the same form as the equilibrium correlations.

A correlation could then be developed that determines the chemical kinetic time as a function of the overall cell fuel air ratio, pressure and temperature. The data was correlated using the same method as previously mentioned for the equilibrium equations. Two correlations for each of the three species, one for the lean side and one for the rich side, were obtained.

Jet-A Mechanism

The following is GLSENS input for the 23 step, 16 species mechanism from Krishna Kundu that was used for the Jet-A calculations.

```
  Jet-A  Mechanism  used in GLSENS
 &RTYPE   GLOBAL=.TRUE., GRONLY=.FALSE.,   &END
  H2      +   OH      =   H2O     +   H          1.17E+11    1.1       3626.
  H2      +   O       =   H       +   OH         2.50E+15     0.       6000.
  H       +   O2      =   O       +   OH         4.00E+14     0.      18000.
  N2      +   O2      >2.0O       +   N2         1.00E+18     0.     122239.
  H2      +2.0O       >   O2      +   H2         5.00E+17     .5          0.
  H2      +2.0H       =2.0H2                     4.00E+20   -1.           0.
  H       +   O2      =   HO2                    1.00E+15   -1.1          0.
  O       +   HO2     =   OH      +   O2         1.50E+13     0.          0.
  H       +   HO2     =   H2      +   O2         1.50E+13     0.          0.
  CO      +   OH      =   CO2     +   H          4.17E+11    0.0       1000.
  CO      +   HO2     >   CO2     +   OH         5.80E+13     0.      22934.
  CH      +   O       =   CO      +   H          1.00E+10     .5          0.
  CH      +   NO      =   CO      +   NH         1.00E+11     0.          0.
  CH      +   O2      =   CO      +   OH         3.00E+10     0.          0.
  C2H2    +   O2      =2.0CO      +   H          3.00E+12     0.      49000.
  N2      +2.0N       =   N2      +   N2         1.00E+15     0.          0.
  N       +   O2      =   NO      +   O          6.30E+09    1.         6300.
  N       +   OH      =   NO      +   H          3.00E+13   0.           0.
  NH      +   O       =   NO      +   H          1.50E+13    0.          0.
  NH      +   NO      =   N2      +   OH         2.00E+15   -.8          0.

   O       +    N2      +    HO2      >2.00NO      +    H       +    O
  .1        .5     1.          1.50E+07   1.      45900.
            2.00NO      +    H        >    N2      +    HO2
            1.1     1.          2.50E+10   .16     8000.
                N2      +    O        >    NO      +    N
             .5     1.          4.75E+10   .29     75010.
                N       +    NO       >    N2      +    O
            1.      1.          3.00E+12   .2         0.
   H2       +    N2      +2.00CH       >2.00CH      +2.00NH
  .1         1.     1.          1.00E+16   0.      78000.
             2.00NH      +2.00CH       >2.00CH      +    N2      +    H2
            2.      1.          1.95E+15   0.         0.
                N2      +    C12H23   >6.00C2H2    +11.0H       +    N2
             .8     .8          2.50E+09   .0      30000.
                N2      +    C12H23   >12.0CH      +11.0H       +    N2
             .8     .8          2.50E+10   .0      30000.
```

For the last three body mechanism step the rate is given by $2.5 \times 10^{10} e^{-30000/RT} N_2^{0.8} C_{12}H_2 3^{0.8}$ in an irreversible step.

Note the fuel is $C_{12}H_{23.}$ The last two steps are irreversible fuel breakup reactions to CH and C_2H_2. The methane reaction must react through free radical attack of O and OH.

Note, some reactions are bimolecular and some are trimolecular expressions. The code follows the method of LSENS developed by Radhakrishnan (Reference 6).

Jet-A Results

The chemical kinetic time equations for Jet-A fuel may be found in Table 3.

Table 3. Jet -A Chemical Kinetic Time Correlations

Species	Lean	Rich
Fuel	$\tau_{fuel} = 3.17e^{-5}(f/a)^{0.272}(P)^{-0.678}\exp[\frac{14446}{T}]$	$\tau_{fuel} = 3.48e^{-5}(f/a)^{0.596}(P)^{-0.639}\exp[\frac{15586}{T}]$
CO	$\tau_{CO} = 0.0591(f/a)^{-0.349}(P)^{-0.743}\exp[\frac{9535}{T}]$	$\tau_{CO} = 0.0654(f/a)^{-0.570}(P)^{-0.781}\exp[\frac{8009}{T}]$
NO_x	$\tau_{NO_x} = 786(f/a)^{-0.28}(P)^{-1.56}\exp[\frac{27513}{T}]$	$\tau_{NO_x} = 981(f/a)^{-0.372}(P)^{-1.61}\exp[\frac{26288}{T}]$

These correlations show that the chemical kinetic time decreases with increasing pressure, resulting in a faster reaction. Parity plots for each chemical kinetic time equation were generated to show how close the simple model value for the chemical kinetic time was to the expected value. These plots can be found in Figures 5-10. The fuel and NO_x plots show a strong correlation, however there is a greater amount of scatter in the *CO* plots. Figures 11-13 show the break in the chemical kinetic time function at an equivalence ratio of one. Concentration versus time is plotted in Figures 14-19 at temperatures of 1500K and 2500K for equivalence ratios of 0.5, 1.0, and 1.5. These plots are a comparison of the concentration given by the full mechanism and the concentration calculated by using the simple models. There was a fairly smooth transition between the lean and rich sides of the reaction.

Auto ignition times using the simple model and a given formula were calculated and compared. The auto ignition time for the simple model is based on the recommendation of reference 7, where the time required for ignition is for 5 percent of the fuel to react.

$$Fuel = F_o e^{-t/\tau} \tag{11}$$

$$\text{If } \frac{Fuel}{F_o} = 0.95 \quad \text{then } \frac{t}{\tau} = 0.051 \quad \text{and} \quad t_{auto\ ignition} = 0.05\tau_{Fuel}. \tag{12}$$

Note that τ_{fuel} decreases as f/a decreases. We used an f/a of 0.02 with the lean equation. The formula for calculating the auto ignition time for Jet-A (reference 8) is given by:

$$\tau P(milli\,\mathrm{sec}\,onds \cdot atm) = 3.4e^{-3}\exp\left[\frac{15300}{RT}\right] \tag{13}$$

Figure 20, a plot of auto ignition time versus temperatures, shows that the auto ignition time given by the simple model is fairly close to the auto ignition time given by the accepted formula. The two curves intersect at approximately 900K and then separate.

This behavior could be due to the fact that the Jet-A reaction mechanism shifts after that temperature. Calculations for the simple model were not done at temperatures below 1000K.

One can use the correlations for computing premixed NO_x levels. The NO_x in parts per million (ppm) or the emission index (EI) can be computed using equation 6.

$$NO_x\left(\frac{mole}{cc}\right)=\frac{t}{\tau_{NO_x}} \tag{14}$$

$\tau_{NOx\ in}$ milliseconds for lean Jet-A is given by the following correlation:

$$\tau_{NO_x}=786\left(\frac{f}{a}\right)^{-0.28}P^{-1.56}exp\left(\frac{27513}{T}\right) \tag{15}$$

At a fuel/air ratio of 0.02, a temperature of 1500K, and a pressure of 5.5 atm, $\tau_{NO_x}=1.52\times10^{10}$ ms. For a typical combustor, the residence time is 2 milliseconds, resulting in the following NO_x concentration:

$$NO_x\frac{moles}{cc}=\frac{2}{1.52\times10^{10}}=1.31\times10^{-10} \tag{16}$$

The concentration in ppm is calculated as follows:

$$NO_x(ppm)=\frac{NO_x\left(\frac{moles}{cc}\right)}{\rho\left(\frac{moles}{cc}\right)}\times10^6 \quad \text{where } \rho=\frac{P}{RT}=4.47\times10^{-5} \tag{17}$$

The NO_x concentration in ppm is then 2.94.

The EI may also be calculated as follows:

$$EI_{No_x}\left(\frac{gm}{1000gmfuel}\right)=\frac{1+\frac{f}{a}}{\frac{f}{a}}\bullet\frac{ppm}{630}=0.24 \tag{18}$$

This result is consistent with the data.

Methane Equations

The following methane chemical kinetic time correlations were obtained:

Table 4. Methane Chemical Kinetic Time Correlations

Species	Lean	Rich
Fuel	$\tau_{fuel} = 2.11e^{-4}(f/a)^{0.400}(P)^{-0.987}\exp[\frac{18942}{T}]$	$\tau_{fuel} = 7.49e^{-4}(f/a)^{0.651}(P)^{-1.0}\exp[\frac{14451}{T}]$
CO	$\tau_{CO} = 1.20(f/a)^{-0.182}(P)^{-1.49}\exp[\frac{-2555}{T}]$	$\tau_{CO}=3.03e^{11}(f/a)^{11.0}(P)^{-1.02}\exp[\frac{6795}{T}]$
NO_x	$\tau_{NO_x} = 9.84e^{-4}(f/a)^{-1.29}(P)^{-0.923}\exp[\frac{37067}{T}]$	$\tau_{NO_x} = 5.32e^{9}(f/a)^{6.15}(P)^{-1.70}\exp[\frac{25538}{T}]$

A detailed discussion of the methane results may be found in Appendix D.

Conclusion

A simplified kinetic scheme for Jet-A and methane fuels resulted in equations relating the chemical kinetic times to overall fuel air ratio, pressure and temperature. The chemical kinetic time equations can then be used in a numerical combustor code to compare the kinetic time with the turbulent mixing time. Fairly strong Jet-A Fuel and methane chemical kinetic time correlations for fuel and NO_x were developed. The *CO* correlation is shown to be not as strong as the others, but all of the twelve equations are believed to be extremely useful in the comparison of kinetic reaction and turbulent mixing times and in the computation of kinetic rate results.

APPENDIX A

Performing Multiple Linear Regression on a Logarithmic Equation

This regression technique may be used to develop a correlation between a dependent variable and one or more independent variables. First the equation to be used must be linearized. An example of an exponential equation used here is shown below.

$$A = BC^c D^d exp\left(\frac{e}{T}\right) \qquad \text{(Non-linear form)} \qquad (19)$$

$$\ln(A) = \ln(B) + c\ln(C) + d\ln(D) + \frac{e}{T} \qquad \text{(Linear form)} \qquad (20)$$

Columns of data containing the independent variables (natural log of C, natural log of D, $1/T$,) and the independent variable (natural log of A) were contained in an Excel spreadsheet. (It is easiest to have the independent variables adjacent to each other, followed by the dependent variable.)

The multiple variable regression analysis is located in the Data Analysis Toolpak. The Data Analysis Toolpak must be added into the spreadsheet if it is not already running in Excel. In order to add it, select the 'Add ins' button from the Tools menu. Click on the Analysis Toolpak option and click OK to accept this choice. Then choose 'Data Analysis' from the Tools menu and double click on 'regression'. Click on the 'Input Y Range' box and highlight the column that contains the logarithm of the dependent variable and press return. Click on the 'Input X Range' box and highlight the columns containing all of the independent variables. (In this case ln(C),ln(D) and $1/T$). Press OK to begin the regression. The regression data will be contained in a new worksheet. The variable labeled 'intercept' will be equal to the natural log of coefficient B. The remaining coefficients (c,d, and e) will be given as X Variable 1,X Variable 2 and X Variable 3 respectively. This process is quick and accurate for Excel 2002 and was used for all equations given in this report.

APPENDIX B

Equilibrium Results

The following equilibrium correlations for oxygen and nitrogen oxide were developed in addition to the *CO* equilibrium values given previously. (Pressure is in atm, Temperature in K, and all concentrations in moles/cc). The following tables show the similarity between the Jet-A and methane equilibrium coefficients.

Table 5. Jet-A Fuel Equilibrium Correlations

	Lean	Rich
O_2	$O_{2eq} = 6.85e^{-10}\left(\frac{f}{a}\right)^{-1.74} P^{0.987}\left[\exp(\frac{1437}{T})\right]$	$O_{2eq} = 2.49e^{-12}\left(\frac{f}{a}\right)^{-12.4} P^{0.101}\left[\exp(\frac{-55989}{T})\right]$
NO_x	$NO_{eq} = 1.47e^{-7}\left(\frac{f}{a}\right)^{-0.913} P^{0.993}\left[\exp(\frac{-9458}{T})\right]$	$NO_{eq} = 5.82e^{-9}\left(\frac{f}{a}\right)^{-6.33} P^{0.551}\left[\exp(\frac{-37899}{T})\right]$

Table 6. Methane Equilibrium Correlations

	Lean	Rich
O_2	$O_{2eq} = 4.53e^{-10}\left(f/a\right)^{-1.77} P^{0.99}\left[\exp(\frac{1468}{T})\right]$	$O_{2eq} = 2.0e^{-13}\left(f/a\right)^{-12.3} P^{0.093}\left[\exp(\frac{-54529}{T})\right]$
NO_x	$NO_{eq} = 1.18e^{-7}\left(f/a\right)^{-0.921} P^{0.995}\left[\exp(\frac{-9419}{T})\right]$	$NO_{eq} = 1.52e^{-9}\left(f/a\right)^{-6.30} P^{0.547}\left[\exp(\frac{-37207}{T})\right]$

APPENDIX C

Methane Mechanism

The following mechanism was used for the methane calculations. It is from GRI.Mech 2.1 (from the GRI.mech website), and it contains 46 species and 247 reactions. The Low/Troe pressure dependence was removed, as this feature was not supported by GLSENS. Only k infinity at the high pressure limit was used. Also 4 species (CH2 (s), NNH, NCO and HCNN) were removed because they were not included in the kinetic thermodynamic data set. Note that the mechanism format below was converted to the GLSENS format prior to using it in GLSENS.

```
! GRI-Mech Version 2.1  released 9/6/95  CHEMKIN-II
format
! See README21 file at anonymous FTP site unix.sri.com, directory
gri;
! WorldWideWeb home page through
http://www.gri.org/tech/res/
!   for additional information, contacts, and disclaimer
REACTIONS
2O+M<=>O2+M                         1.200E+17   -1.000
.00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/
O+H+M<=>OH+M                         5.000E+17   -1.000       .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
O+H2<=>H+OH                         5.000E+04    2.670    6290.00
O+HO2<=>OH+O2                        2.000E+13     .000       .00
O+H2O2<=>OH+HO2                      9.630E+06    2.000    4000.00
O+CH<=>H+CO                         5.700E+13     .000       .00
O+CH2<=>H+HCO                        8.000E+13     .000       .00
O+CH2(S)<=>H2+CO                     1.500E+13     .000       .00
O+CH2(S)<=>H+HCO                     1.500E+13     .000       .00
O+CH3<=>H+CH2O                       8.430E+13     .000       .00
O+CH4<=>OH+CH3                       1.020E+09    1.500    8600.00
O+CO+M<=>CO2+M                       6.020E+14     .000    3000.00
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/
O+HCO<=>OH+CO                        3.000E+13     .000       .00
O+HCO<=>H+CO2                        3.000E+13     .000       .00
O+CH2O<=>OH+HCO                      3.900E+13     .000    3540.00
O+CH2OH<=>OH+CH2O                    1.000E+13     .000       .00
O+CH3O<=>OH+CH2O                     1.000E+13     .000       .00
O+CH3OH<=>OH+CH2OH                   3.880E+05    2.500    3100.00
O+CH3OH<=>OH+CH3O                    1.300E+05    2.500    5000.00
O+C2H<=>CH+CO                        5.000E+13     .000       .00
O+C2H2<=>H+HCCO                      1.020E+07    2.000    1900.00
O+C2H2<=>OH+C2H                      4.600E+19   -1.410   28950.00
O+C2H2<=>CO+CH2                      1.020E+07    2.000    1900.00
O+C2H3<=>H+CH2CO                     3.000E+13     .000       .00
O+C2H4<=>CH3+HCO                     1.920E+07    1.830     220.00
O+C2H5<=>CH3+CH2O                    1.320E+14     .000       .00
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O+C2H6<=>OH+C2H5                    8.980E+07    1.920    5690.00
O+HCCO<=>H+2CO                      1.000E+14     .000       .00
O+CH2CO<=>OH+HCCO                   1.000E+13     .000    8000.00
O+CH2CO<=>CH2+CO2                   1.750E+12     .000    1350.00
O2+CO<=>O+CO2                       2.500E+12     .000   47800.00
O2+CH2O<=>HO2+HCO                   1.000E+14     .000   40000.00
H+O2+M<=>HO2+M                      2.800E+18    -.860       .00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/
H+2O2<=>HO2+O2                      3.000E+20   -1.720       .00
H+O2+H2O<=>HO2+H2O                  9.380E+18    -.760       .00
H+O2+N2<=>HO2+N2                    3.750E+20   -1.720       .00
H+O2<=>O+OH                         8.300E+13     .000   14413.00
2H+M<=>H2+M                         1.000E+18   -1.000       .00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/
2H+H2<=>2H2                         9.000E+16    -.600       .00
2H+H2O<=>H2+H2O                     6.000E+19   -1.250       .00
2H+CO2<=>H2+CO2                     5.500E+20   -2.000       .00
H+OH+M<=>H2O+M                      2.200E+22   -2.000       .00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/
H+HO2<=>O+H2O                       3.970E+12     .000     671.00
H+HO2<=>O2+H2                       2.800E+13     .000    1068.00
H+HO2<=>2OH                         1.340E+14     .000     635.00
H+H2O2<=>HO2+H2                     1.210E+07    2.000    5200.00
H+H2O2<=>OH+H2O                     1.000E+13     .000    3600.00
H+CH<=>C+H2                         1.100E+14     .000       .00
H+CH2(+M)<=>CH3(+M)                 2.500E+16    -.800       .00
    LOW  / 3.200E+27   -3.140   1230.00/
    TROE/   .6800   78.00  1995.00  5590.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH2(S)<=>CH+H2                    3.000E+13     .000       .00
H+CH3(+M)<=>CH4(+M)                 1.270E+16    -.630     383.00
    LOW  / 2.477E+33   -4.760   2440.00/
    TROE/   .7830   74.00  2941.00  6964.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH4<=>CH3+H2                      6.600E+08    1.620   10840.00
H+HCO(+M)<=>CH2O(+M)                1.090E+12     .480    -260.00
    LOW  / 1.350E+24   -2.570   1425.00/
    TROE/   .7824  271.00  2755.00  6570.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+HCO<=>H2+CO                       7.340E+13     .000       .00
H+CH2O(+M)<=>CH2OH(+M)              5.400E+11     .454    3600.00
    LOW  / 1.270E+32   -4.820   6530.00/
    TROE/   .7187  103.00  1291.00  4160.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH2O(+M)<=>CH3O(+M)               5.400E+11     .454    2600.00
    LOW  / 2.200E+30   -4.800   5560.00/
    TROE/   .7580   94.00  1555.00  4200.00 /
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H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH2O<=>HCO+H2                    2.300E+10    1.050    3275.00
H+CH2OH(+M)<=>CH3OH(+M)             1.800E+13     .000       .00
    LOW  / 3.000E+31   -4.800   3300.00/
    TROE/   .7679  338.00  1812.00  5081.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH2OH<=>H2+CH2O                   2.000E+13     .000       .00
H+CH2OH<=>OH+CH3                    1.200E+13     .000       .00
H+CH2OH<=>CH2(S)+H2O                6.000E+12     .000       .00
H+CH3O(+M)<=>CH3OH(+M)              5.000E+13     .000       .00
    LOW  / 8.600E+28   -4.000   3025.00/
    TROE/   .8902  144.00  2838.00 45569.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+CH3O<=>H+CH2OH                    3.400E+06    1.600       .00
H+CH3O<=>H2+CH2O                    2.000E+13     .000       .00
H+CH3O<=>OH+CH3                     3.200E+13     .000       .00
H+CH3O<=>CH2(S)+H2O                 1.600E+13     .000       .00
H+CH3OH<=>CH2OH+H2                  1.700E+07    2.100    4870.00
H+CH3OH<=>CH3O+H2                   4.200E+06    2.100    4870.00
H+C2H(+M)<=>C2H2(+M)                1.000E+17   -1.000       .00
    LOW  / 3.750E+33   -4.800   1900.00/
    TROE/   .6464  132.00  1315.00  5566.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+C2H2(+M)<=>C2H3(+M)                5.600E+12     .000    2400.00
    LOW  / 3.800E+40   -7.270   7220.00/
    TROE/   .7507   98.50  1302.00  4167.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+C2H3(+M)<=>C2H4(+M)                6.080E+12     .270     280.00
    LOW  / 1.400E+30   -3.860   3320.00/
    TROE/   .7820  207.50  2663.00  6095.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+C2H3<=>H2+C2H2                    3.000E+13     .000       .00
H+C2H4(+M)<=>C2H5(+M)                1.080E+12     .454    1820.00
    LOW  / 1.200E+42   -7.620   6970.00/
    TROE/   .9753  210.00   984.00  4374.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+C2H4<=>C2H3+H2                    1.325E+06    2.530   12240.00
H+C2H5(+M)<=>C2H6(+M)                5.210E+17    -.990    1580.00
    LOW  / 1.990E+41   -7.080   6685.00/
    TROE/   .8422  125.00  2219.00  6882.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H+C2H5<=>H2+C2H4                    2.000E+12     .000       .00
H+C2H6<=>C2H5+H2                    1.150E+08    1.900    7530.00
H+HCCO<=>CH2(S)+CO                   1.000E+14     .000       .00
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H+CH2CO<=>HCCO+H2                   5.000E+13    .000    8000.00
H+CH2CO<=>CH3+CO                    1.130E+13    .000    3428.00
H+HCCOH<=>H+CH2CO                   1.000E+13    .000       .00
H2+CO(+M)<=>CH2O(+M)                4.300E+07   1.500   79600.00
    LOW  /  5.070E+27   -3.420  84350.00/
    TROE/   .9320  197.00  1540.00 10300.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
OH+H2<=>H+H2O                       2.160E+08   1.510    3430.00
2OH(+M)<=>H2O2(+M)                  7.400E+13   -.370       .00
    LOW  /  2.300E+18   -.900  -1700.00/
    TROE/   .7346   94.00  1756.00  5182.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
2OH<=>O+H2O                         3.570E+04   2.400   -2110.00
OH+HO2<=>O2+H2O                     2.900E+13    .000    -500.00
OH+H2O2<=>HO2+H2O                   1.750E+12    .000     320.00
 DUPLICATE
OH+H2O2<=>HO2+H2O                   5.800E+14    .000    9560.00
 DUPLICATE
OH+C<=>H+CO                         5.000E+13    .000       .00
OH+CH<=>H+HCO                       3.000E+13    .000       .00
OH+CH2<=>H+CH2O                     2.000E+13    .000       .00
OH+CH2<=>CH+H2O                     1.130E+07   2.000    3000.00
OH+CH2(S)<=>H+CH2O                  3.000E+13    .000       .00
OH+CH3(+M)<=>CH3OH(+M)              6.300E+13    .000       .00
    LOW  /  2.700E+38   -6.300   3100.00/
    TROE/   .2105   83.50  5398.00  8370.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
OH+CH3<=>CH2+H2O                    5.600E+07   1.600    5420.00
OH+CH3<=>CH2(S)+H2O                 2.501E+13    .000       .00
OH+CH4<=>CH3+H2O                    1.000E+08   1.600    3120.00
OH+CO<=>H+CO2                       4.760E+07   1.228      70.00
OH+HCO<=>H2O+CO                     5.000E+13    .000       .00
OH+CH2O<=>HCO+H2O                   3.430E+09   1.180    -447.00
OH+CH2OH<=>H2O+CH2O                 5.000E+12    .000       .00
OH+CH3O<=>H2O+CH2O                  5.000E+12    .000       .00
OH+CH3OH<=>CH2OH+H2O                1.440E+06   2.000    -840.00
OH+CH3OH<=>CH3O+H2O                 6.300E+06   2.000    1500.00
OH+C2H<=>H+HCCO                     2.000E+13    .000       .00
OH+C2H2<=>H+CH2CO                   2.180E-04   4.500   -1000.00
OH+C2H2<=>H+HCCOH                   5.040E+05   2.300   13500.00
OH+C2H2<=>C2H+H2O                   3.370E+07   2.000   14000.00
OH+C2H2<=>CH3+CO                    4.830E-04   4.000   -2000.00
OH+C2H3<=>H2O+C2H2                  5.000E+12    .000       .00
OH+C2H4<=>C2H3+H2O                  3.600E+06   2.000    2500.00
OH+C2H6<=>C2H5+H2O                  3.540E+06   2.120     870.00
OH+CH2CO<=>HCCO+H2O                 7.500E+12    .000    2000.00
2HO2<=>O2+H2O2                      1.300E+11    .000   -1630.00
 DUPLICATE
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2HO2<=>O2+H2O2                    4.200E+14     .000   12000.00
 DUPLICATE
HO2+CH2<=>OH+CH2O                  2.000E+13     .000       .00
HO2+CH3<=>O2+CH4                   1.000E+12     .000       .00
HO2+CH3<=>OH+CH3O                  2.000E+13     .000       .00
HO2+CO<=>OH+CO2                    1.500E+14     .000   23600.00
HO2+CH2O<=>HCO+H2O2                1.000E+12     .000    8000.00
C+O2<=>O+CO                       5.800E+13     .000     576.00
C+CH2<=>H+C2H                      5.000E+13     .000
.00
C+CH3<=>H+C2H2                     5.000E+13     .000       .00
CH+O2<=>O+HCO                      3.300E+13     .000       .00
CH+H2<=>H+CH2                      1.107E+08    1.790    1670.00
CH+H2O<=>H+CH2O                    1.713E+13     .000    -755.00
CH+CH2<=>H+C2H2                    4.000E+13     .000       .00
CH+CH3<=>H+C2H3                    3.000E+13     .000       .00
CH+CH4<=>H+C2H4                    6.000E+13     .000       .00
CH+CO(+M)<=>HCCO(+M)               5.000E+13     .000       .00
    LOW  / 2.690E+28   -3.740   1936.00/
    TROE/   .5757  237.00  1652.00  5069.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
CH+CO2<=>HCO+CO                    3.400E+12     .000     690.00
CH+CH2O<=>H+CH2CO                  9.460E+13     .000    -515.00
CH+HCCO<=>CO+C2H2                  5.000E+13     .000       .00
CH2+O2<=>OH+HCO                    1.320E+13     .000    1500.00
CH2+H2<=>H+CH3                     5.000E+05    2.000    7230.00
2CH2<=>H2+C2H2                     3.200E+13     .000
.00
CH2+CH3<=>H+C2H4                   4.000E+13     .000       .00
CH2+CH4<=>2CH3                     2.460E+06    2.000    8270.00
CH2+CO(+M)<=>CH2CO(+M)             8.100E+11     .500    4510.00
    LOW  / 2.690E+33   -5.110   7095.00/
    TROE/   .5907  275.00  1226.00  5185.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
CH2+HCCO<=>C2H3+CO                 3.000E+13     .000       .00
CH2(S)+N2<=>CH2+N2                 1.500E+13     .000     600.00
CH2(S)+O2<=>H+OH+CO                2.800E+13     .000       .00
CH2(S)+O2<=>CO+H2O                 1.200E+13     .000       .00
CH2(S)+H2<=>CH3+H                  7.000E+13     .000       .00
CH2(S)+H2O(+M)<=>CH3OH(+M)         2.000E+13     .000       .00
    LOW  / 2.700E+38   -6.300   3100.00/
    TROE/   .1507  134.00  2383.00  7265.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
CH2(S)+H2O<=>CH2+H2O               3.000E+13     .000       .00
CH2(S)+CH3<=>H+C2H4                1.200E+13     .000    -570.00
CH2(S)+CH4<=>2CH3                  1.600E+13     .000    -570.00
CH2(S)+CO<=>CH2+CO                 9.000E+12     .000       .00
CH2(S)+CO2<=>CH2+CO2               7.000E+12     .000       .00
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CH2(S)+CO2<=>CO+CH2O                  1.400E+13     .000        .00
CH2(S)+C2H6<=>CH3+C2H5                4.000E+13     .000    -550.00
CH3+O2<=>O+CH3O                      2.675E+13     .000   28800.00
CH3+O2<=>OH+CH2O                      3.600E+10     .000    8940.00
CH3+H2O2<=>HO2+CH4                    2.450E+04    2.470    5180.00
2CH3(+M)<=>C2H6(+M)                   2.120E+16    -.970     620.00
    LOW  /  1.770E+50   -9.670   6220.00/
    TROE/   .5325  151.00  1038.00  4970.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
2CH3<=>H+C2H5                        4.990E+12     .100   10600.00
CH3+HCO<=>CH4+CO                      2.648E+13     .000        .00
CH3+CH2O<=>HCO+CH4                    3.320E+03    2.810    5860.00
CH3+CH3OH<=>CH2OH+CH4                 3.000E+07    1.500
9940.00
CH3+CH3OH<=>CH3O+CH4                  1.000E+07    1.500    9940.00
CH3+C2H4<=>C2H3+CH4                   2.270E+05    2.000    9200.00
CH3+C2H6<=>C2H5+CH4                   6.140E+06    1.740   10450.00
HCO+H2O<=>H+CO+H2O                    2.244E+18   -1.000   17000.00
 DUPLICATE
HCO+M<=>H+CO+M                       1.870E+17   -1.000   17000.00
H2/2.00/ H2O/ .00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
 DUPLICATE
HCO+O2<=>HO2+CO                      7.600E+12     .000     400.00
CH2OH+O2<=>HO2+CH2O                   1.800E+13     .000     900.00
CH3O+O2<=>HO2+CH2O                    4.280E-13    7.600   -3530.00
C2H+O2<=>HCO+CO                      5.000E+13     .000    1500.00
C2H+H2<=>H+C2H2                      4.070E+05    2.400     200.00
C2H3+O2<=>HCO+CH2O                    3.980E+12     .000    -240.00
C2H4(+M)<=>H2+C2H2(+M)                8.000E+12     .440   88770.00
    LOW  /  7.000E+50   -9.310  99860.00/
    TROE/   .7345  180.00  1035.00  5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
C2H5+O2<=>HO2+C2H4                    8.400E+11     .000    3875.00
HCCO+O2<=>OH+2CO                      1.600E+12     .000     854.00
2HCCO<=>2CO+C2H2                     1.000E+13     .000        .00
N+NO<=>N2+O                          3.500E+13     .000     330.00
N+O2<=>NO+O                          2.650E+12     .000    6400.00
N+OH<=>NO+H                          7.333E+13     .000    1120.00
N2O+O<=>N2+O2                         1.400E+12     .000   10810.00
N2O+O<=>2NO                          2.900E+13     .000   23150.00
N2O+H<=>N2+OH                         4.400E+14     .000   18880.00
N2O+OH<=>N2+HO2                       2.000E+12     .000   21060.00
N2O(+M)<=>N2+O(+M)                    1.300E+11     .000   59620.00
    LOW  /  6.200E+14     .000  56100.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
HO2+NO<=>NO2+OH                       2.110E+12     .000    -480.00
NO+O+M<=>NO2+M                       1.060E+20   -1.410        .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
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C2H6/3.00/
NO2+O<=>NO+O2                       3.900E+12    .000   -240.00
NO2+H<=>NO+OH                       1.320E+14    .000    360.00
NH+O<=>NO+H                         5.000E+13    .000       .00
NH+H<=>N+H2                         3.200E+13    .000
330.00
NH+OH<=>HNO+H                       2.000E+13    .000       .00
NH+OH<=>N+H2O                       2.000E+09   1.200       .00
NH+O2<=>HNO+O                       4.610E+05   2.000   6500.00
NH+O2<=>NO+OH                       1.280E+06   1.500    100.00
NH+N<=>N2+H                         1.500E+13    .000       .00
NH+H2O<=>HNO+H2                     2.000E+13    .000  13850.00
NH+NO<=>N2+OH                       2.160E+13   -.230       .00
NH+NO<=>N2O+H                       4.160E+14   -.450       .00
NH2+O<=>OH+NH                       7.000E+12    .000       .00
NH2+O<=>H+HNO                       4.600E+13    .000       .00
NH2+H<=>NH+H2                       4.000E+13    .000   3650.00
NH2+OH<=>NH+H2O                     9.000E+07   1.500   -460.00
NNH<=>N2+H                          3.300E+08    .000       .00
 DUPLICATE
NNH+M<=>N2+H+M                      1.300E+14   -.110   4980.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
 DUPLICATE
NNH+O2<=>HO2+N2                     5.000E+12    .000       .00
NNH+O<=>OH+N2                       2.500E+13    .000       .00
NNH+O<=>NH+NO                       7.000E+13    .000       .00
NNH+H<=>H2+N2                       5.000E+13    .000
.00
NNH+OH<=>H2O+N2                     2.000E+13    .000       .00
NNH+CH3<=>CH4+N2                    2.500E+13    .000       .00
H+NO+M<=>HNO+M                      8.950E+19   -1.320    740.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
HNO+O<=>NO+OH                       2.500E+13    .000       .00
HNO+H<=>H2+NO                       4.500E+11    .720    660.00
HNO+OH<=>NO+H2O                     1.300E+07   1.900   -950.00
HNO+O2<=>HO2+NO                     1.000E+13    .000  13000.00
CN+O<=>CO+N                         7.700E+13    .000       .00
CN+OH<=>NCO+H                       4.000E+13    .000       .00
CN+H2O<=>HCN+OH                     8.000E+12    .000   7460.00
CN+O2<=>NCO+O                       6.140E+12    .000   -440.00
CN+H2<=>HCN+H                       2.100E+13    .000   4710.00
NCO+O<=>NO+CO                       2.350E+13    .000       .00
NCO+H<=>NH+CO                       5.400E+13    .000       .00
NCO+OH<=>NO+H+CO                    2.500E+12    .000       .00
NCO+N<=>N2+CO                       2.000E+13    .000       .00
NCO+O2<=>NO+CO2                     2.000E+12    .000  20000.00
NCO+M<=>N+CO+M                      8.800E+16   -.500  48000.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
```

```
NCO+NO<=>N2O+CO                      2.850E+17   -1.520     740.00
NCO+NO<=>N2+CO2                      5.700E+18   -2.000     800.00
HCN+M<=>H+CN+M                       1.040E+29   -3.300  126600.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
HCN+O<=>NCO+H                        1.107E+04    2.640    4980.00
HCN+O<=>NH+CO                        2.767E+03    2.640    4980.00
HCN+O<=>CN+OH                        2.134E+09    1.580   26600.00
HCN+OH<=>HOCN+H                      1.100E+06    2.030   13370.00
HCN+OH<=>HNCO+H                      4.400E+03    2.260    6400.00
HCN+OH<=>NH2+CO                      1.600E+02    2.560    9000.00
H+HCN+M<=>H2CN+M                     1.400E+26   -3.400    1900.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
H2CN+N<=>N2+CH2                      6.000E+13     .000     400.00
C+N2<=>CN+N                          6.300E+13     .000   46020.00
CH+N2<=>HCN+N                        2.857E+08    1.100   20400.00
CH+N2(+M)<=>HCNN(+M)                 3.100E+12     .150       .00
    LOW  /  1.300E+25   -3.160    740.00/
    TROE/   .6670  235.00  2117.00  4536.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
C2H6/3.00/
CH2+N2<=>HCN+NH                      1.000E+13     .000   74000.00
CH2(S)+N2<=>NH+HCN                   1.000E+11     .000   65000.00
C+NO<=>CN+O                          1.900E+13     .000       .00
C+NO<=>CO+N                          2.900E+13     .000       .00
CH+NO<=>HCN+O                        5.000E+13     .000       .00
CH+NO<=>H+NCO                        2.000E+13     .000       .00
CH+NO<=>N+HCO                        3.000E+13     .000       .00
CH2+NO<=>H+HNCO                      3.100E+17   -1.380    1270.00
CH2+NO<=>OH+HCN                      2.900E+14    -.690     760.00
CH2+NO<=>H+HCNO                      3.800E+13    -.360     580.00
CH2(S)+NO<=>H+HNCO                   3.100E+17   -1.380    1270.00
CH2(S)+NO<=>OH+HCN                   2.900E+14    -.690     760.00
CH2(S)+NO<=>H+HCNO                   3.800E+13    -.360     580.00
CH3+NO<=>HCN+H2O                     9.600E+13     .000   28800.00
CH3+NO<=>H2CN+OH                     1.000E+12     .000   21750.00
HCNN+O<=>CO+H+N2                     2.200E+13     .000       .00
HCNN+O<=>HCN+NO                      2.000E+12     .000       .00
HCNN+O2<=>O+HCO+N2                   1.200E+13     .000       .00
HCNN+OH<=>H+HCO+N2                   1.200E+13     .000       .00
HCNN+H<=>CH2+N2                      1.000E+14     .000       .00
HNCO+O<=>NH+CO2                      9.800E+07    1.410    8500.00
HNCO+O<=>HNO+CO                      1.500E+08    1.570   44000.00
HNCO+O<=>NCO+OH                      2.200E+06    2.110   11400.00
HNCO+H<=>NH2+CO                      2.250E+07    1.700    3800.00
HNCO+H<=>H2+NCO                      1.050E+05    2.500   13300.00
HNCO+OH<=>NCO+H2O                    4.650E+12     .000    6850.00
HNCO+OH<=>NH2+CO2                    1.550E+12     .000    6850.00
HNCO+M<=>NH+CO+M                     1.180E+16     .000   84720.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/
```

```
C2H6/3.00/
HCNO+H<=>H+HNCO                    2.100E+15   -.690   2850.00
HCNO+H<=>OH+HCN                    2.700E+11    .180   2120.00
HCNO+H<=>NH2+CO                    1.700E+14   -.750   2890.00
HOCN+H<=>H+HNCO                    2.000E+07   2.000   2000.00
HCCO+NO<=>HCNO+CO                   2.350E+13    .000      .00
CH3+N<=>H2CN+H                    6.100E+14   -.310    290.00
CH3+N<=>HCN+H2                    3.700E+12    .150    -90.00
NH3+H<=>NH2+H2                   5.400E+05   2.400   9915.00
NH3+OH<=>NH2+H2O                   5.000E+07   1.600    955.00
NH3+O<=>NH2+OH                    9.400E+06   1.940   6460.00
END
```

Note the fuel was CH_4. The NO_x was computed as the sum of NO, N_2O and NO_2 or

$$\frac{dNOx}{dt} = \left(\frac{dNO}{dt} + 2 * \frac{dN_2O}{dt} + \frac{dNO_2}{dt} \right) = \frac{1}{\tau_{NOx}} . \tag{21}$$

APPENDIX D

Methane Results

Figures 21 and 22 are parity plots showing the strength of the lean and rich equilibrium correlations for *CO*. These charts show very strong *CO* equilibrium correlations for methane, similar to those for the Jet-A fuel.

The chemical kinetic time correlations developed for methane may be found in Table (4). Parity plots for the chemical kinetic times are given in Figures 23-28. Values on the x-axis represent chemical kinetic times in milliseconds calculated in GLSENS using the complete mechanism, and values on the y-axis represent chemical kinetic times calculated by this report's simple model. The fuel and NO_x parity plots show a fairly tight fitting curve, with a minimal amount of scattering. The *CO* parity plots show a larger amount of scattering. However, the resulting correlations are still believed to be useful in calculating the chemical kinetic times at various sets of conditions.

APPENDIX E

GLSENS Modification

The following lines were added to the GLSENS code for calculation of the chemical kinetic times.

```
C   These lines were added to GLSENS.F in subroutine OUT2 at line
C     7057
C    jetgl.f  7/30/03 for the Jet-A fuel
      timil=time*1.e+03
420   foa=eratio*0.068
      tn=timil
      trr=sngl(T)
      if(foa.ge.0.068)goto 419
      ccoe=4.43*(FOA)**(1.69)*P**0.513*exp(-31840./Trr)
      goto 418
  419 ccoe=5.85E-3*foa**3.82*P**0.961*exp(-969./Trr)
C  Initialize variables at time = 0.
  418 if(time.gt.0.)goto 427
      write(10,1)
    1 format(' nc   P atm   T K   f/a   jeta fuel   co       nox
     3coequil  time')
C     calculate the initial conditions for the averaging
      nc=1
      nco=1
      t0=0.
      stco=0.
      areaf=0.
      tauco=0.
      tauf=0.
      tauno=0.
      areaco=0.
      areano=0.
      atauf=0.
      atauco=0.
      atauno=0.
  427 continue
C  Allow a startup time for the integration.  Begin averaging at
C  nc=15
      if(nc.eq.15)t0=timil
C  Species number from the mechanism are CO=9, NO=12, C12H23=16
      cco=sngl(dabs(prc(9)))
      cnox=sngl(dabs(prc(12)))
      cfuel=sngl(dabs(prc(16)))
      if(nc/1*1.eq.nc)write(10,423)nc,P,T,foa,cfuel,cco,cnox,ccoe,
     1timil
  423 format(i6,f6.1,f8.1,1p,8e10.3)
C     calculate the initial conditions for the averaging
      if(nc.lt.15)goto 1500
C The average kinetic times for the fuel, CO and NO are atauf,
C  atauco, and atauno
      if(W(16).ne.0.)tauf=-sngl(prc(16)/W(16))*1.e3
      if(nc.eq.15)tstart=timil
      if(nc.eq.15)t0=timil
      if(nc.eq.15)taufo=-sngl(prc(16)/W(16))*1.e3
```

```
      if(tn.eq.t0)goto 424
      if(tauf.le.0.)goto 424
      if(cfuel.lt.1.e-14)goto 424
      areaf=areaf+(1./taufo+1./tauf)/2.*(tn-t0)
      timet=timil-tstart
      atauf=timet/areaf
      if(nc/1*1.eq.nc)write(11,423)nc,P,T,foa,cfuel,tauf,atauf,
     1timil
      taufo=tauf
  424 if(nc.eq.15)tauni=sngl(1.D0/(W(12)))*1.e3
      tauno=sngl(1.D0/(W(12)))*1.e3
      if(t0.eq.tn)goto 339
      if(tauno.lt.0.)go to 339
      areano=areano+(1./tauno+1./tauni)/2.*(tn-t0)
      atauno=timet/areano
      tauni=tauno
      if((nc/1*1).eq.nc)write(13,501)nc,P,T,foa,cnox,tauno,
     1atauno,timil,eratio
  339 rfuel=12.*cfuel/tauf*1.e3
C Since co goes to co2,  use the rate of reaction to CO2 (species
C     10) for the rate of conversion of CO
      denm=-sngl(w(10))
C  If we want to average only after the peak, remove the comment C
C     from the next line.
C     if(denm.gt.0.)goto 503
      if(stco.eq.0.)tauci=-(sngl(dabs(prc(9)))-ccoe)/denm*1.e3
      tauco=-(sngl(dabs(prc(9)))-ccoe)/denm*1.e3
C     w(10) = CO2
      if (W(10).lt.0.)next=.true.
      if(t0.eq.tn) goto 504
      if(tauci.le.0.)goto 503
      if(tauco.le.0.)goto 503
      if(stco.eq.0.)stco=timil
      timco=timil-stco
      areaco=areaco+(1./tauco+1./tauci)/2.*(tn-t0)
      atauco=timco/areaco
      tauci=tauco
      nco=nco+1
  338 format(i7,1e12.3,7e12.4)
      if(nc.lt.100)write(15,338)nc,timil,cco,ccoe,w(9),w(10),
     1tauco
      rfuel2=12.*sngl(w(16))
      dcodt=-((sngl(prc(9)))-ccoe)/tauco*1.e3
  503 if((nc/1*1).eq.nc)write(12,423)nc,P,T,foa,cco,ccoe,tauco,
     1atauco,timil
  504 t0=tn
  431 format (f12.2,3e13.5,f8.3,f8.3,e13.5)
      IF(NCO.GT.300)NEXT=.TRUE.
      if(timil.gt.1000.)next=.true.
  501 format(i4,f7.4,f7.1,5e11.3,f6.3)
 1500 nc=nc+1
      if(nc.gt.300)next=.true.
C     if (nc/50*50.ne.nc)go to 502
      DO 435 IJ=1,MAX
      IF (IJ.GT.LS.OR.IJ.GT.LR) GO TO 435
      TCON(IJ)=SNGL(PRC(IJ)/W(IJ))
      FMOL=SNGL(SIGMA(IJ)*MIXMW)
```

```
      WRITE (LWRITE,175) DSPNM(IJ),PRC(IJ),FMOL,W(IJ)
      GO TO 435
430   WRITE (LWRITE,185) IJ,RATE(IJ),PRX(IJ),EQUIL(IJ)
C430   continue
435   CONTINUE
C  The variables atauf, atauco and atauno are saved in a common
C  block and printed in main after the completion of the complete
C  time integration as ln(foa), ln(p), 1./T, Ln(atauf),
C  ln(atauco), and ln(atauno) for processing by Excel regression

502   IF (WELSTR) GO TO 446
C     WRITE (LWRITE,440) DSNAM(1),FF(LSP1),DSNAM(2),FF(LSP2)
440   FORMAT (/,4X,'DERIVATIVES (CGS UNITS): ',2(A8,4X,1PE12.5,4X))
```

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2. Penko, P.F.; Kundu, K.P.; Siow, Y.K.; and Yang, S.L.: A Kinetic Mechanism for Calculation of Pollutant Species in Jet-A Combustion, AIAA 2000–3035
3. Kundu, K.P.; Penko, P.F.; and VanOverbeke, T.J.: A Practical Mechanism for Computing Combustion in Gas Turbine Engines, AIAA 99–2218
4. Bittker, D.A., GLSENS, A Generalized Extension of LSENS Including Global Reactions and Added Sensitivity Analysis for the Perfectly Stirred Reactor, NASA Reference Publication 1362, 1999.
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7. Huber, Paul W.; Schexnayder, Jr., Charles J.; and McClinton, Charles R.: Criteria for Self-Ignition of Supersonic Hydrogen-Air Mixtures, NASA TP–1457, 1979.
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Figure 1
Magnussen Mixing Model

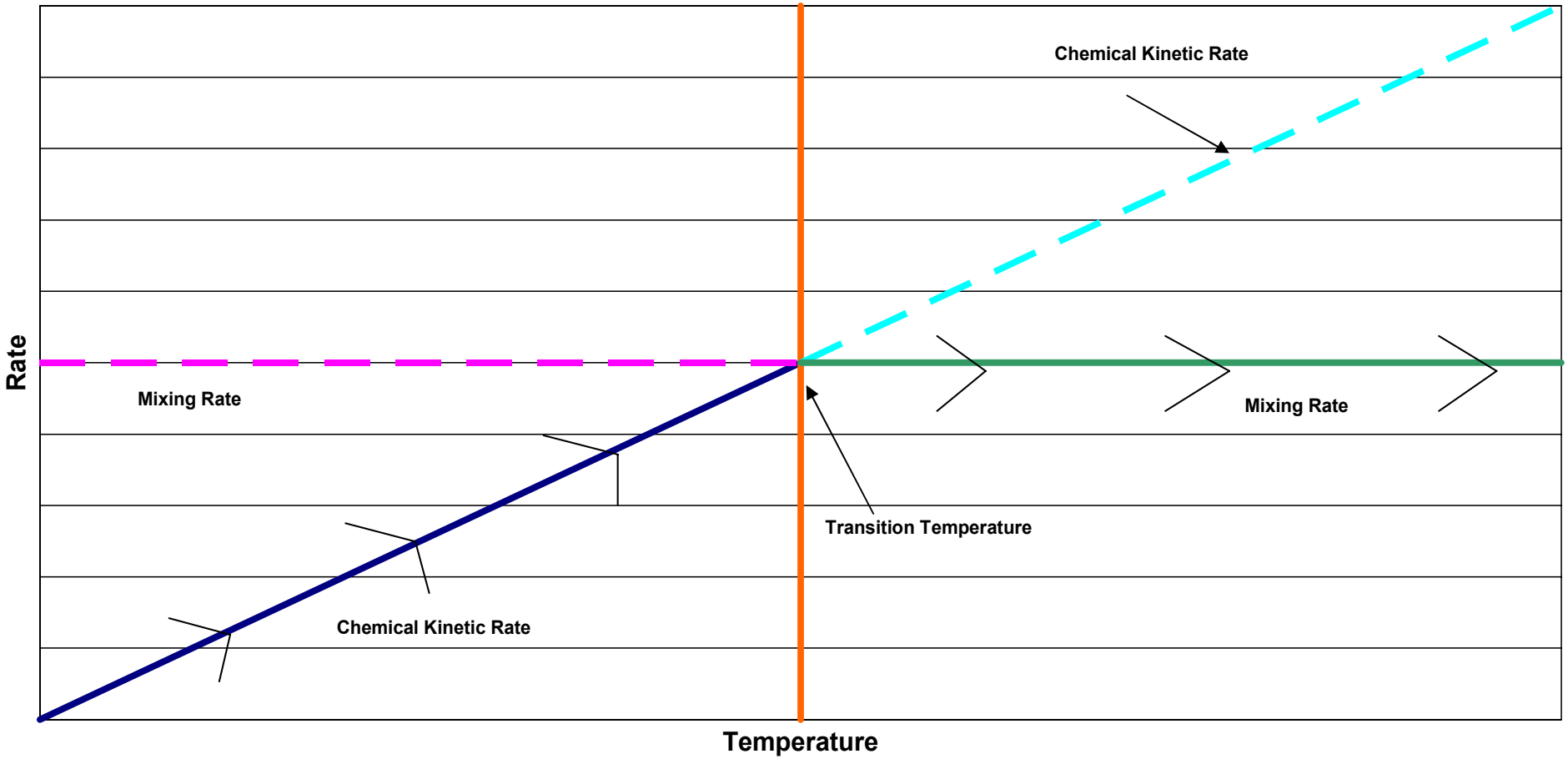


Figure 2
Jet A
CO Equilibrium
Correlation Comparison

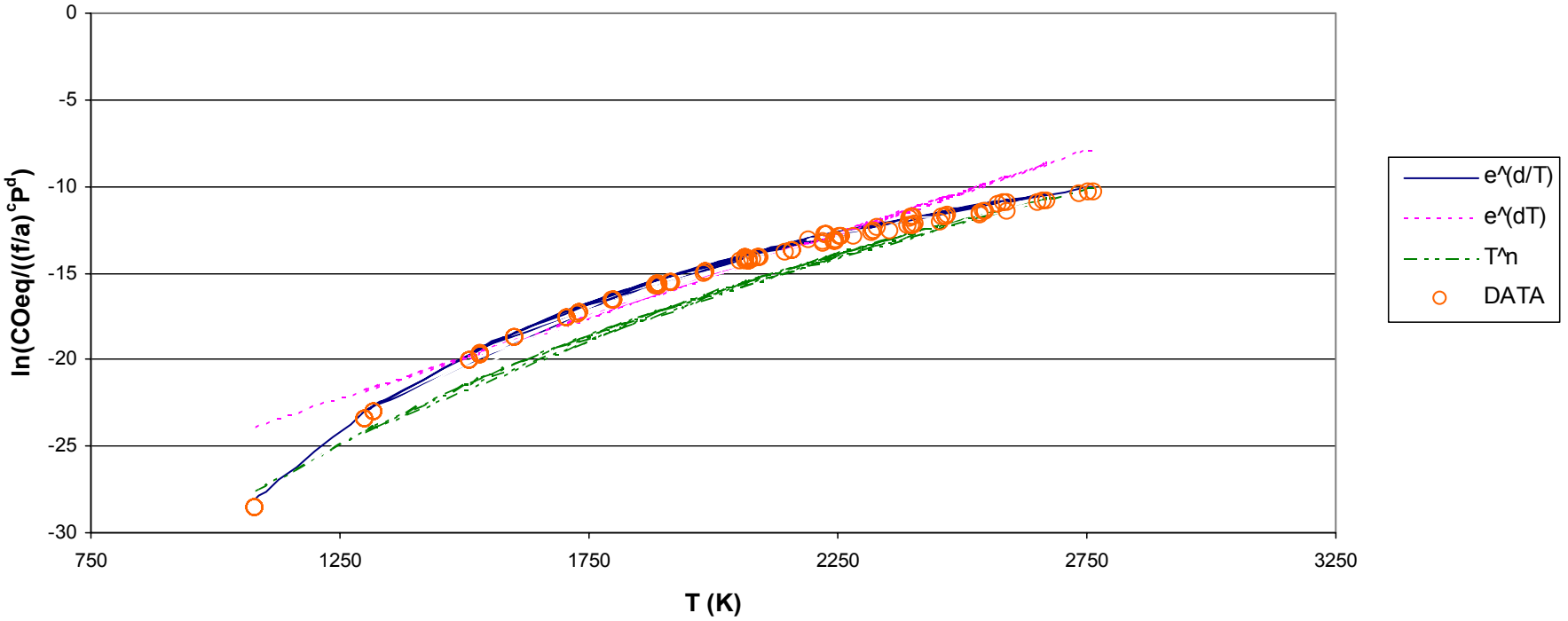


Figure 3 COeq Correlation
Jet-A1 Fuel
f/a <0.068
$Coeq = 4.43(f/a)^{1.69}(P)^{0.513}(\exp[-31840/T])$

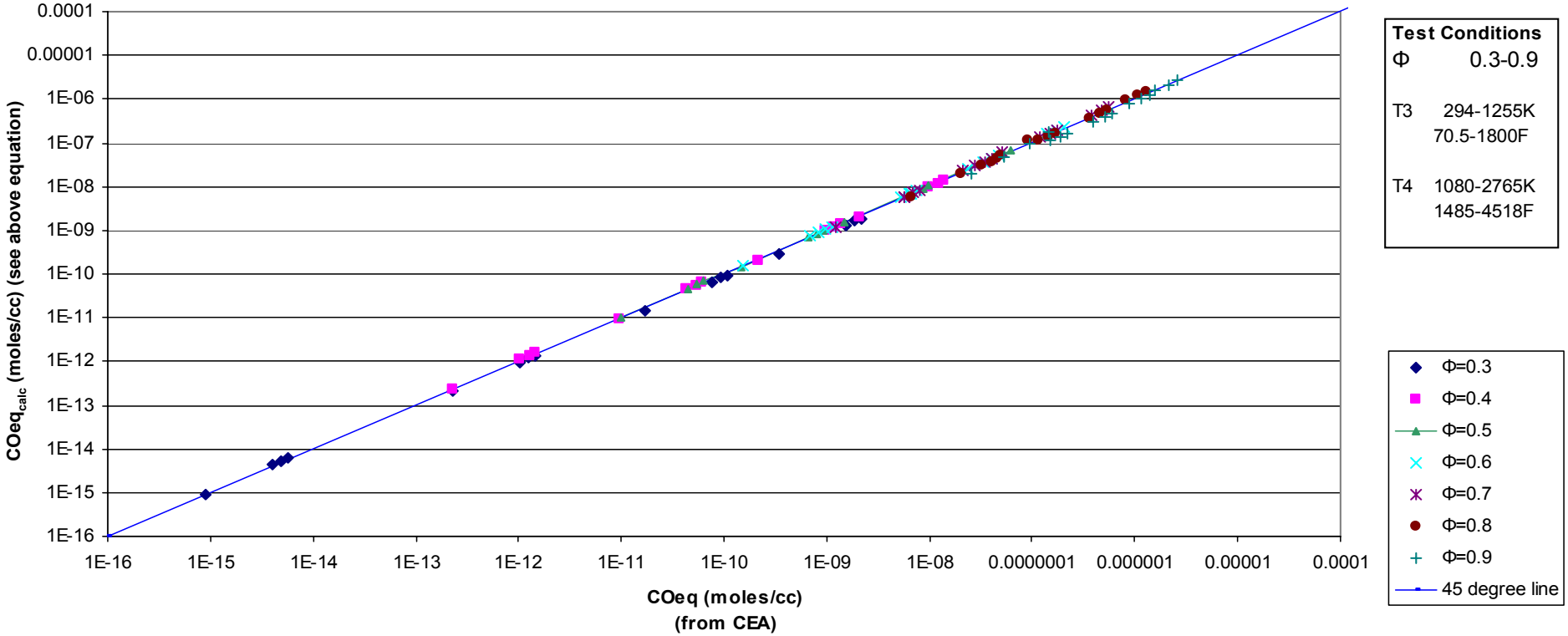


Figure 4 COeq Correlation
Jet-A1 Fuel
f/a ≥ 0.068
$Coeq = 5.85e^{-3}(f/a)^{3.82}(P)^{0.961}(\exp[-969/T])$

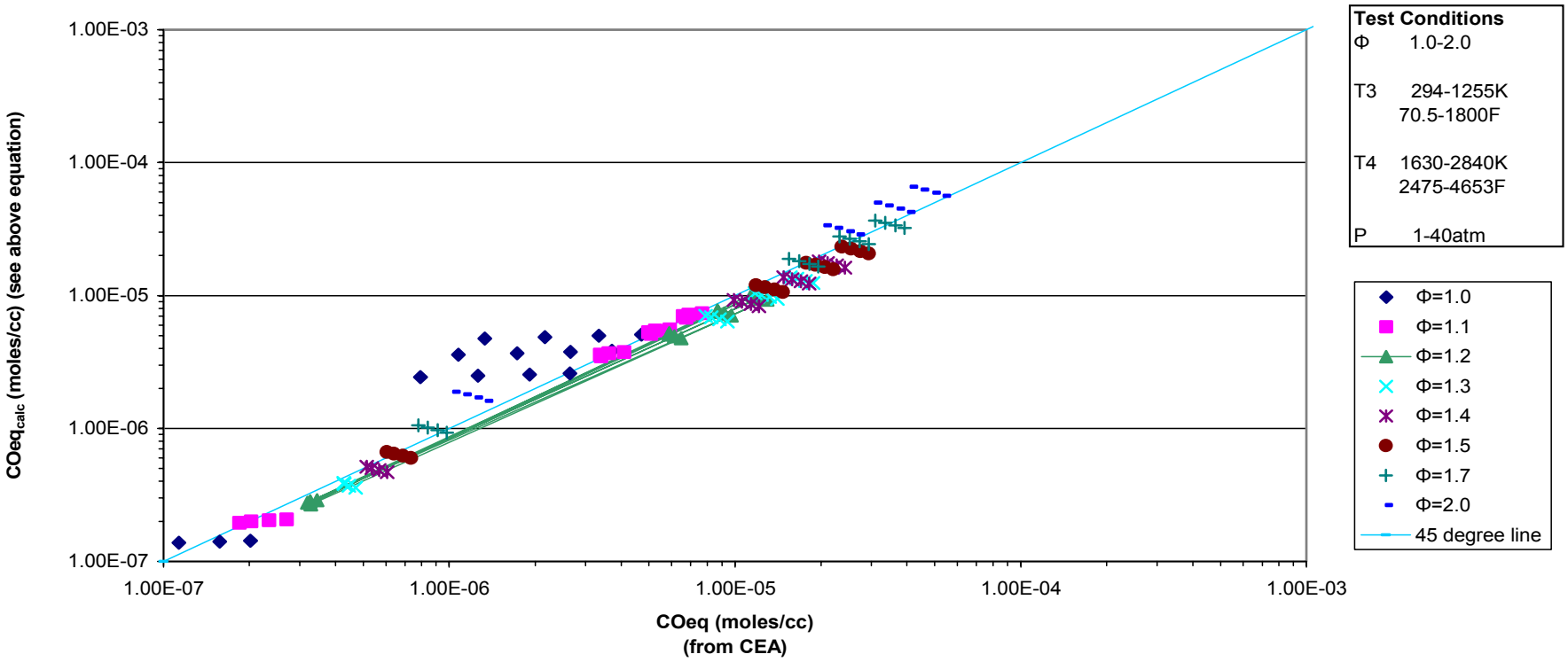


Figure 5 Jet A Fuel tau Parity
(lean 7/29)

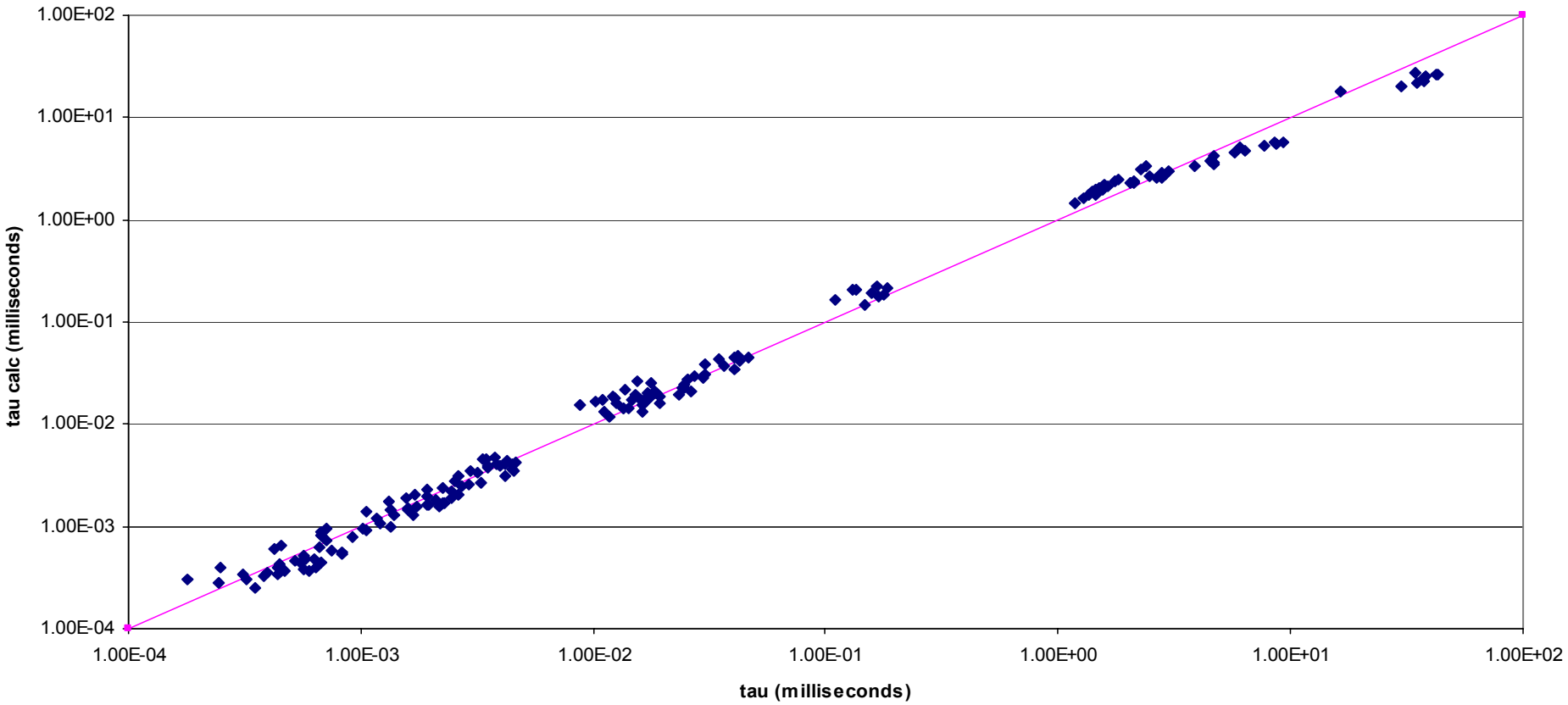


Figure 6 Jet A Fuel Tau Parity
(rich 7/29)

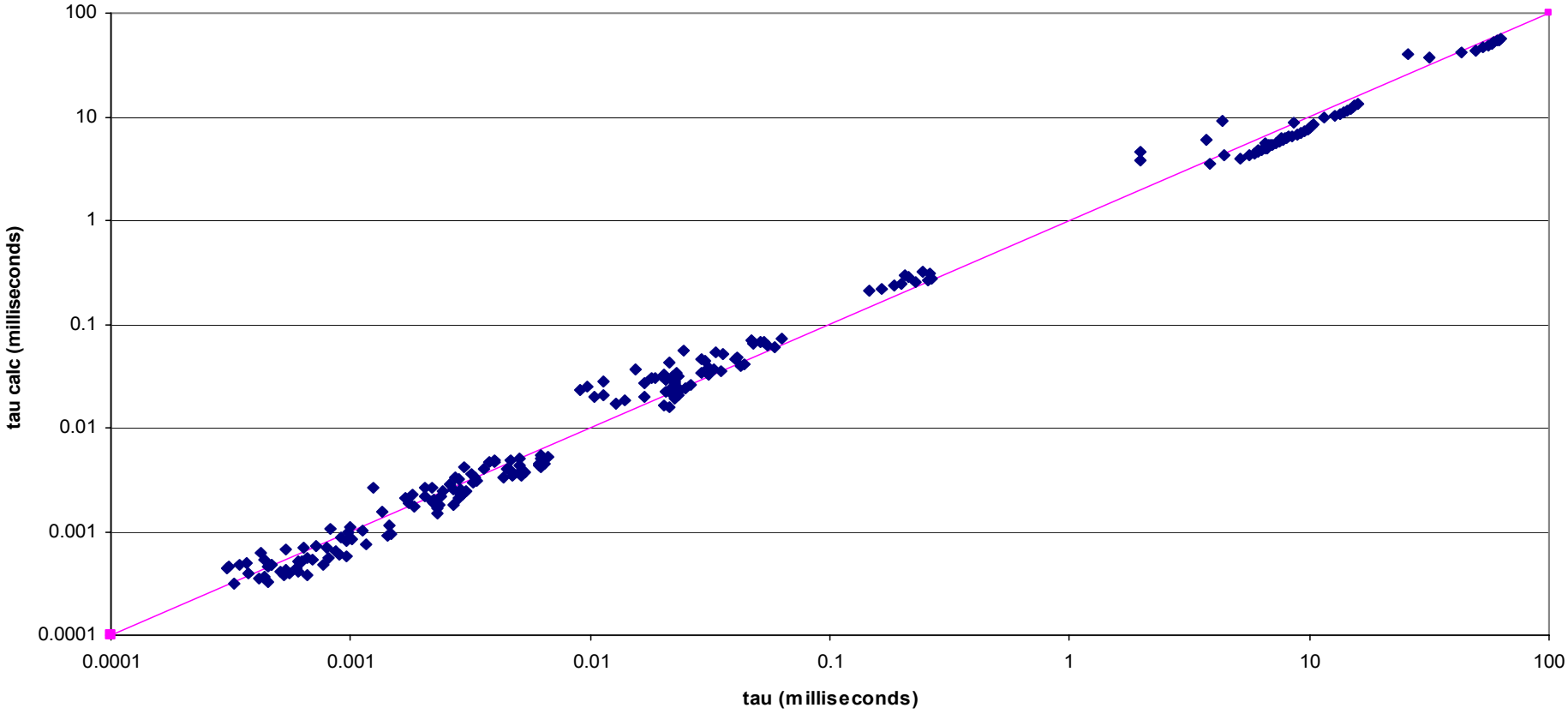


Figure 7
Jet-A CO Tau Parity
(lean 8/18)

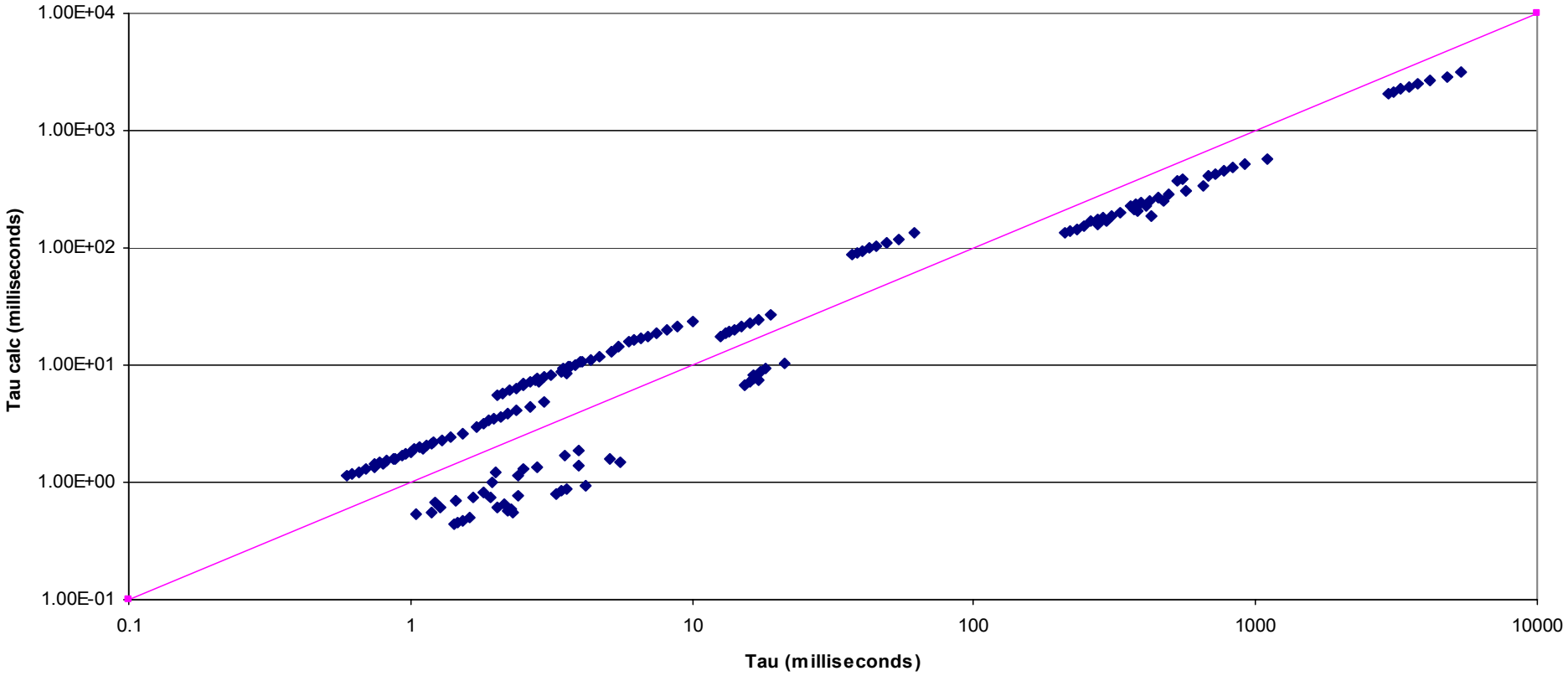


Figure 8
Jet-A CO Tau Parity
(rich 8/18)

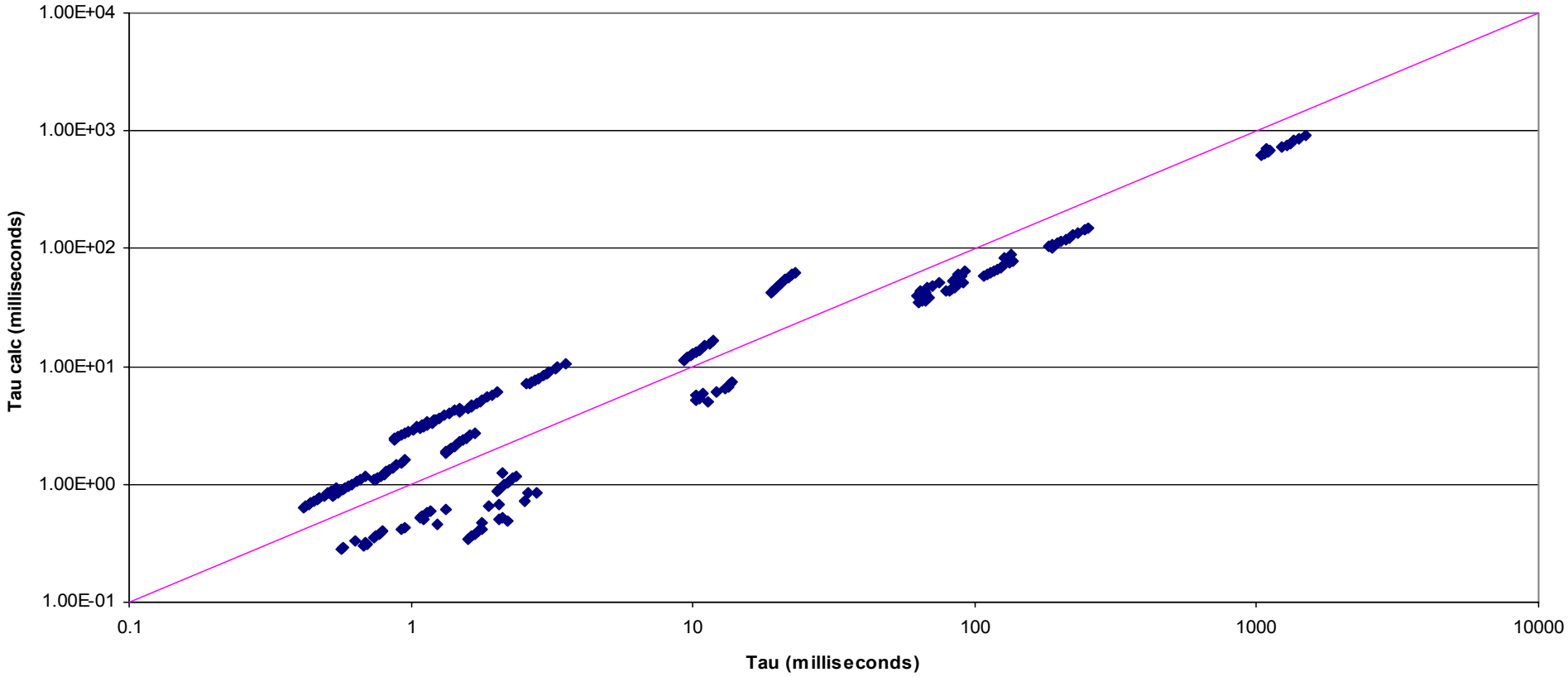


Figure 9 Jet A Nox Tau Parity
(lean 8/5)

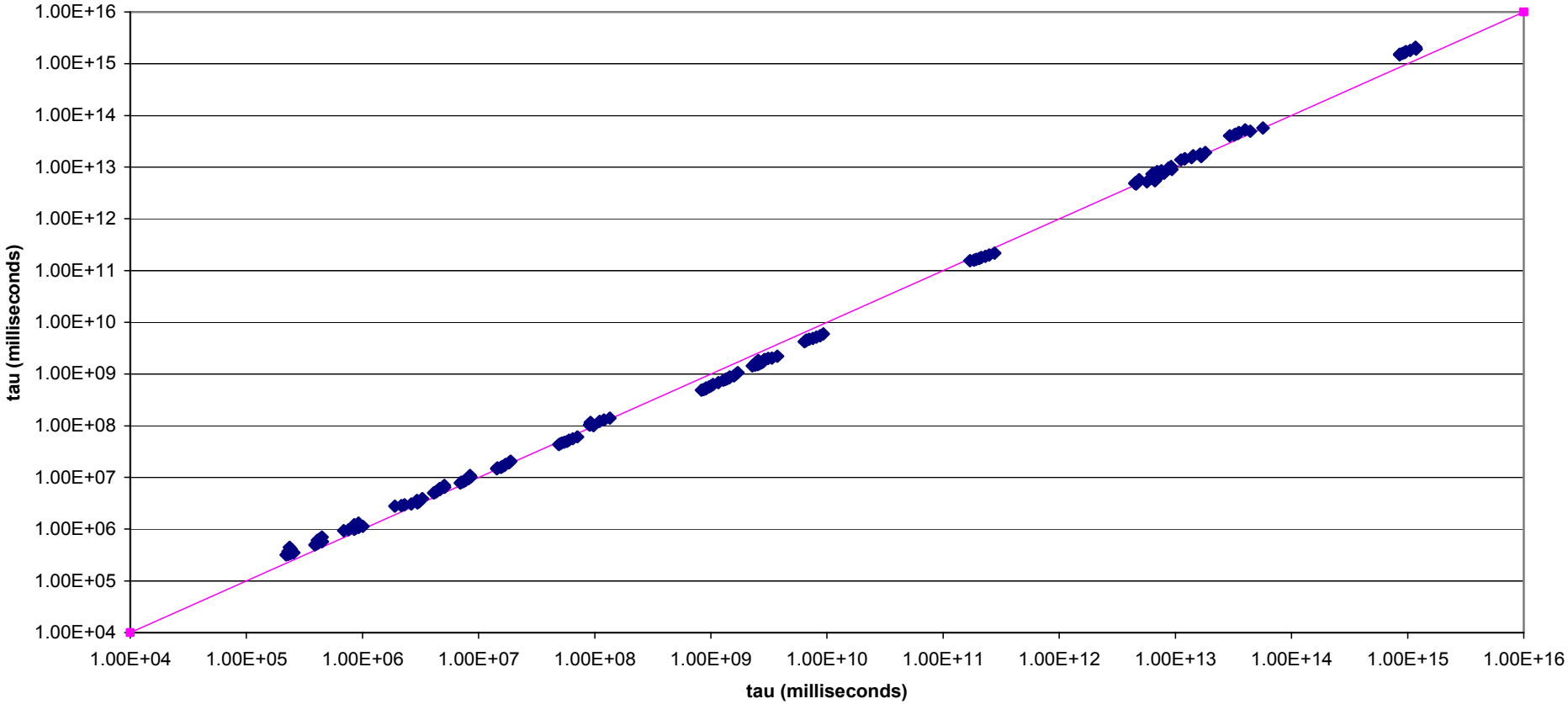


Figure 10 Jet A NOx Tau Parity
(rich 8/5)

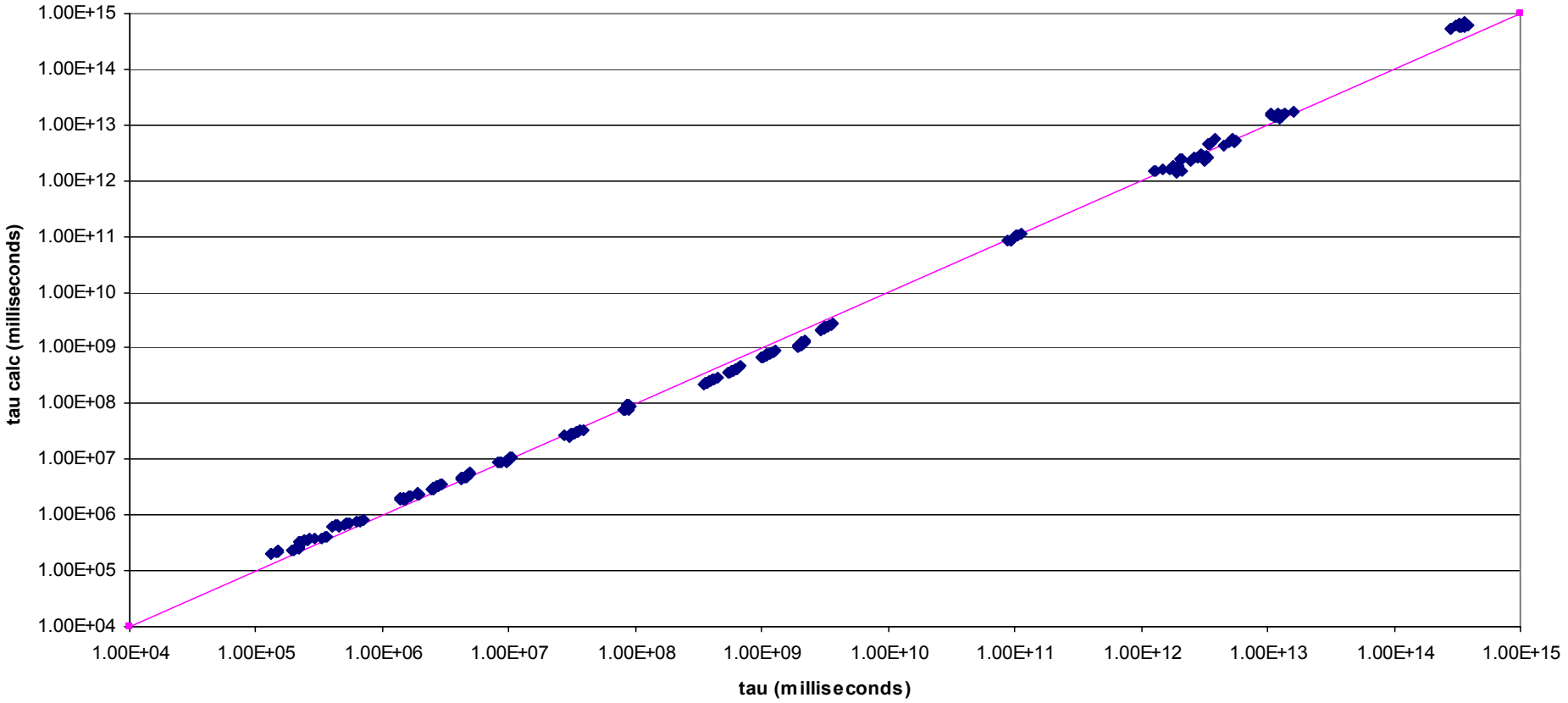


Figure 11
Jet A Fuel

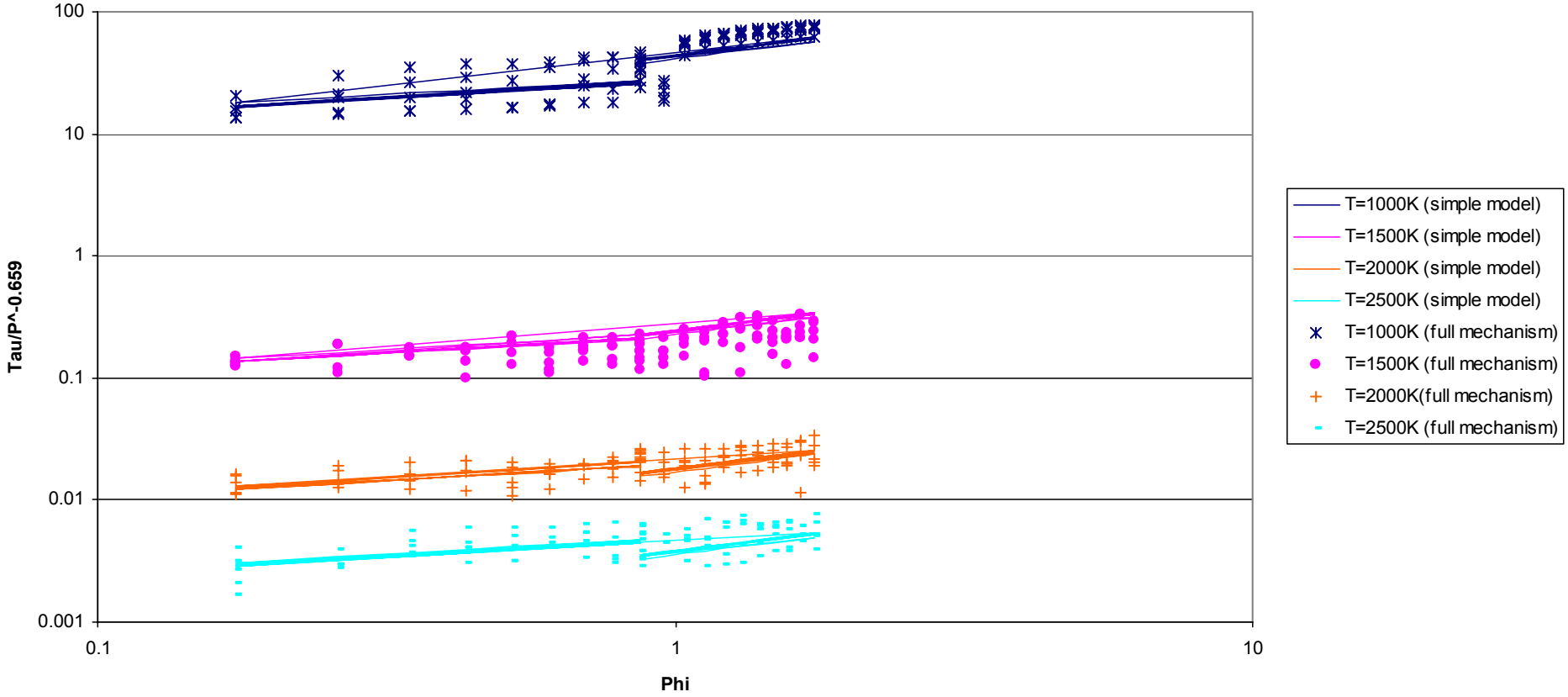


Figure 12
Jet-A CO Tau Correlation

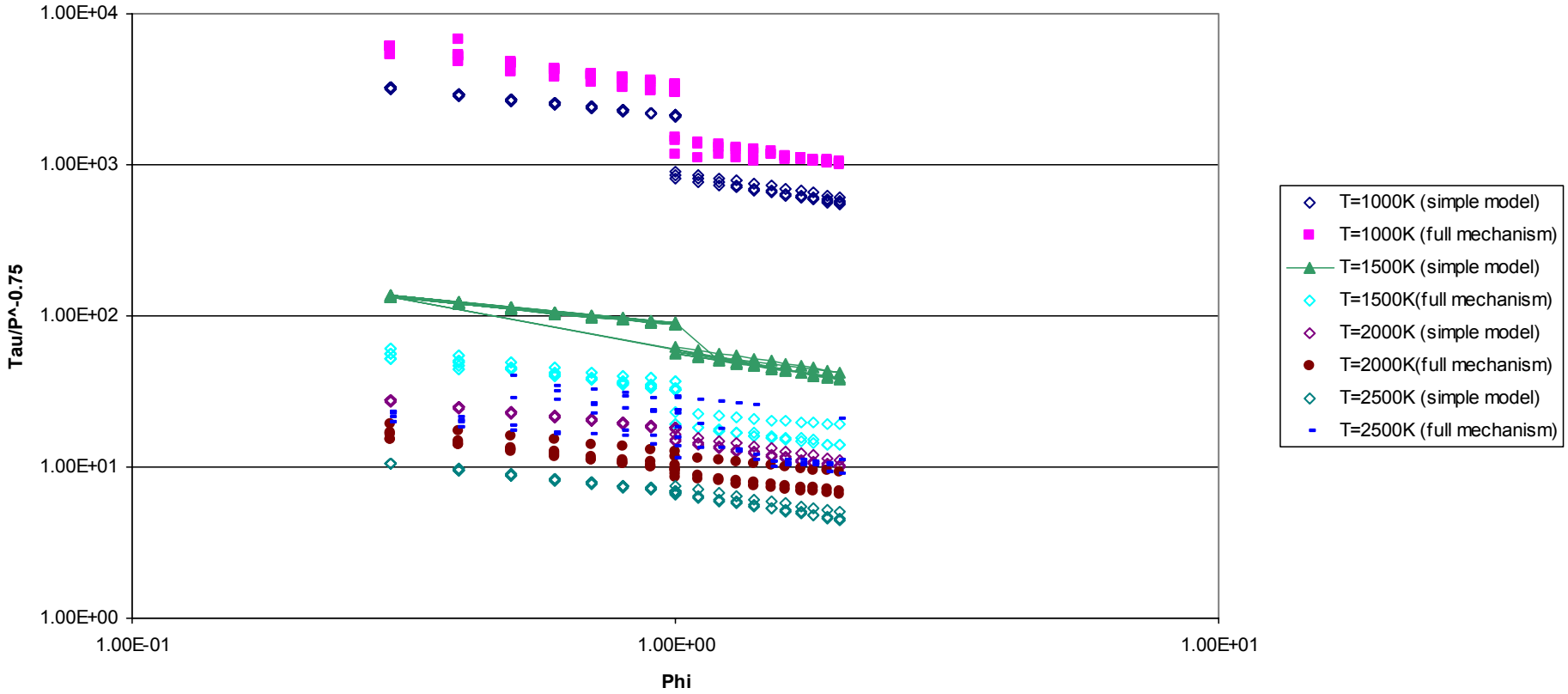


Figure 13
Jet A Fuel NOx

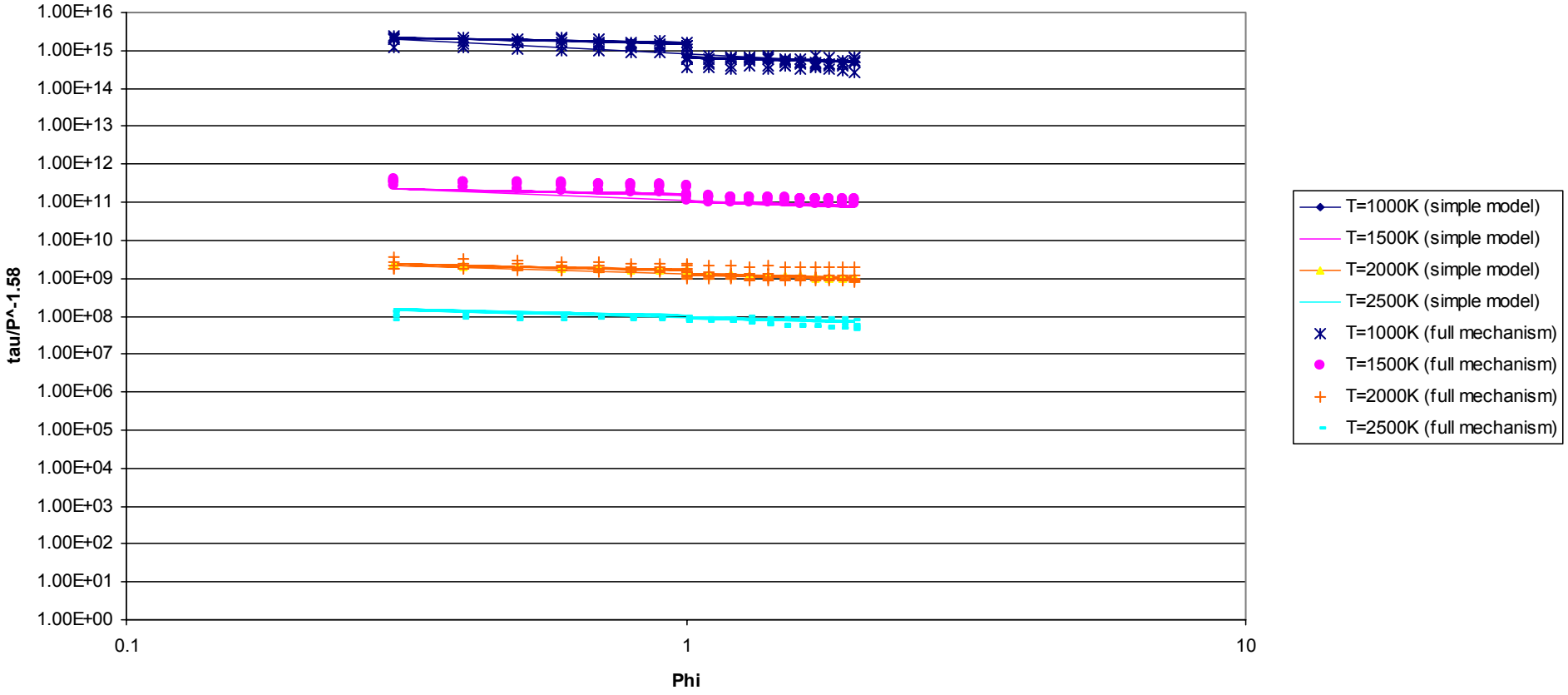


Figure 14
Jet A Fuel
(phi=0.5, T=1500K, P=1atm)

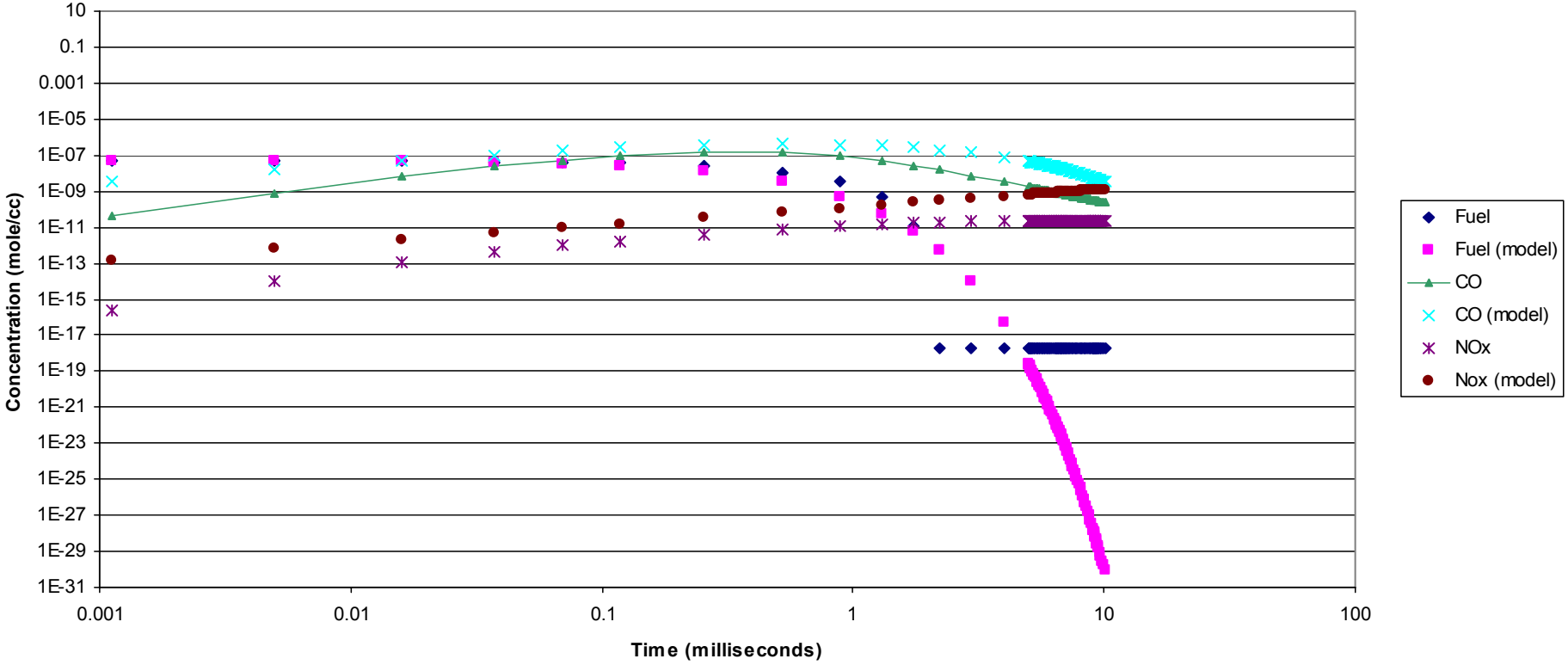


Figure 15
Jet A Fuel
(phi=0.5, T=2500K, P=1atm)

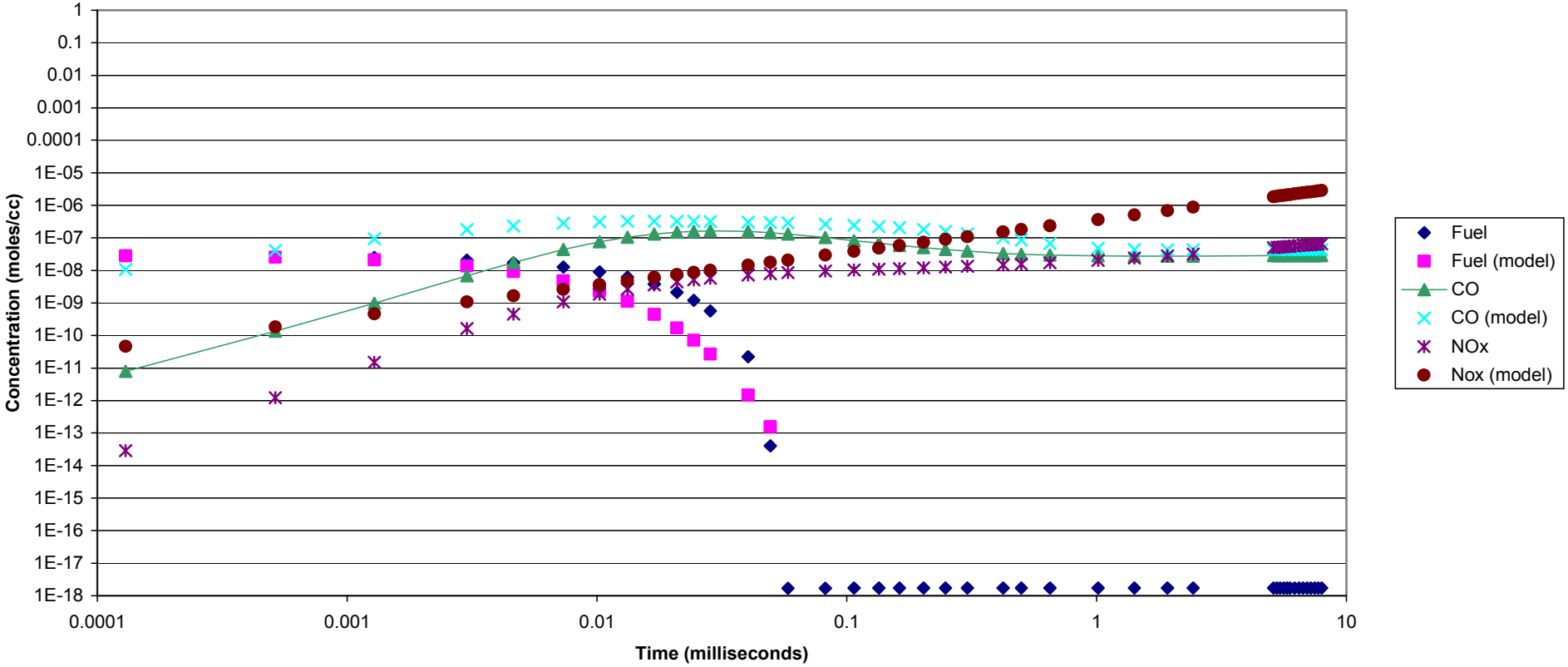


Figure 16
Jet A Fuel
(Phi=1.0, T=1500K,P=1atm)

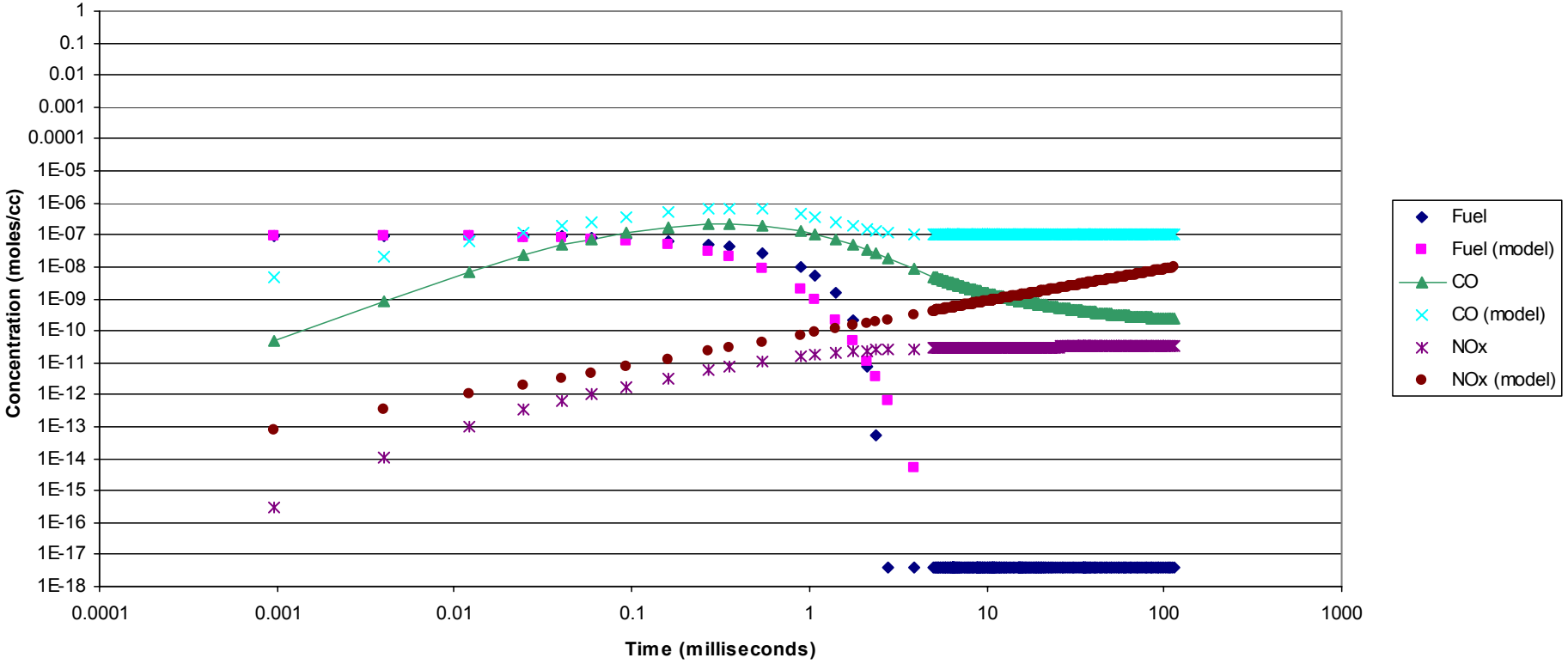


Figure 17
Jet A Fuel
(Phi=1.0, T=2500K, P=1atm)

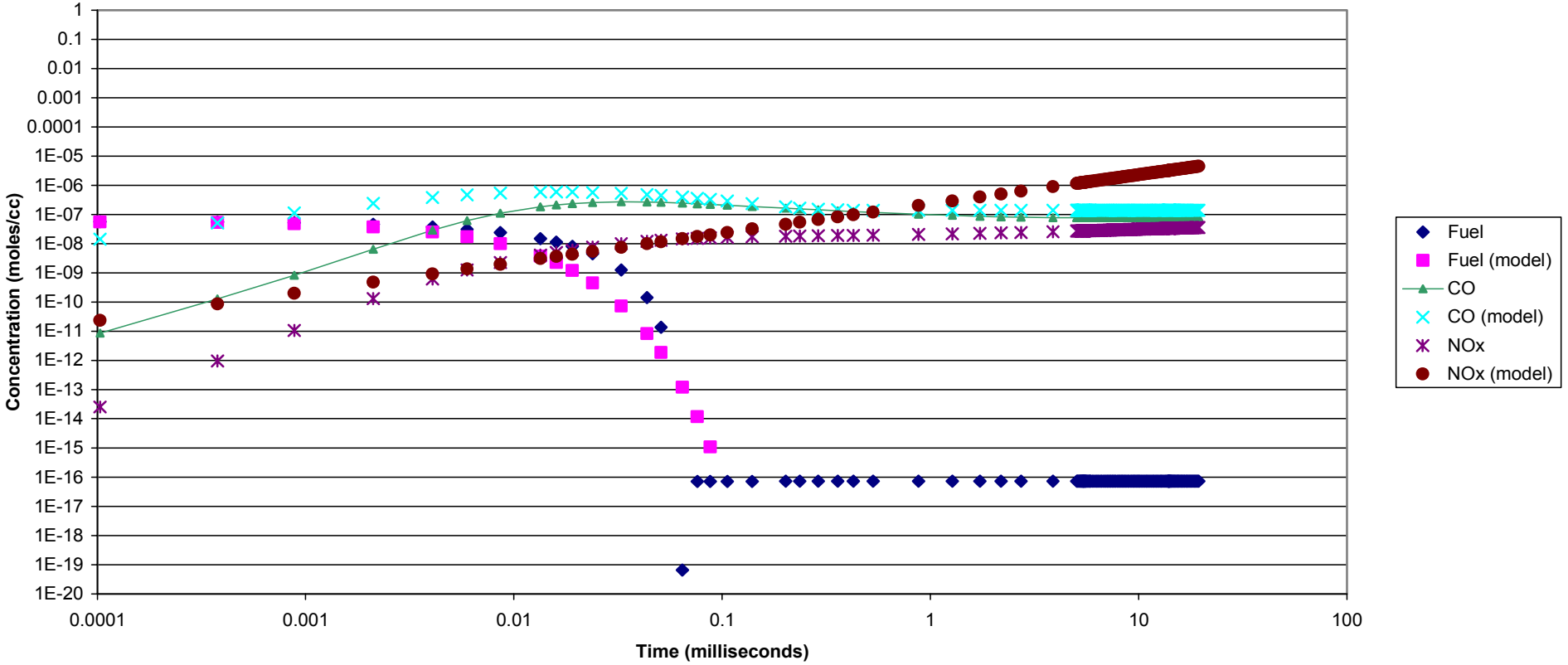


Figure 18
Jet A Fuel
(phi=1.5, T=1500K, P=1atm)

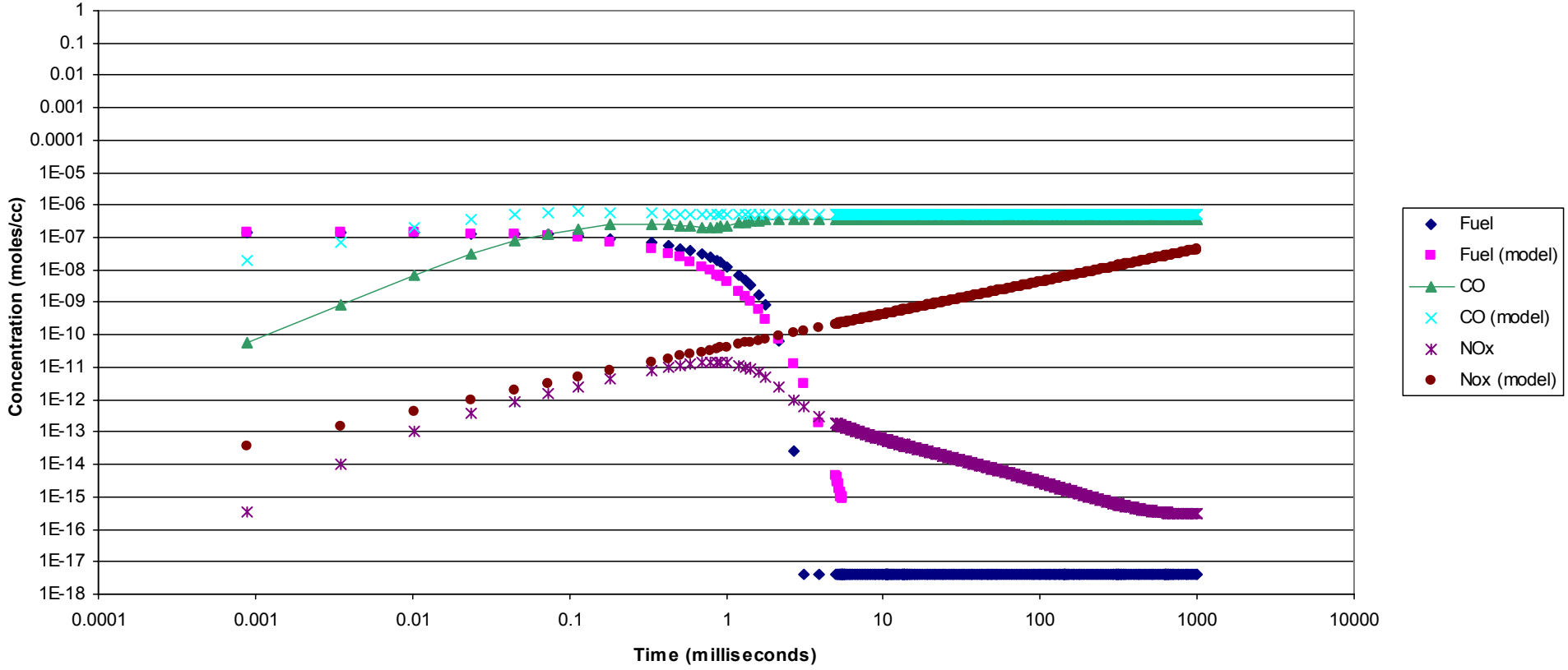


Figure 19
Jet A Fuel
(phi=1.5, T=2500K, P=1 atm)

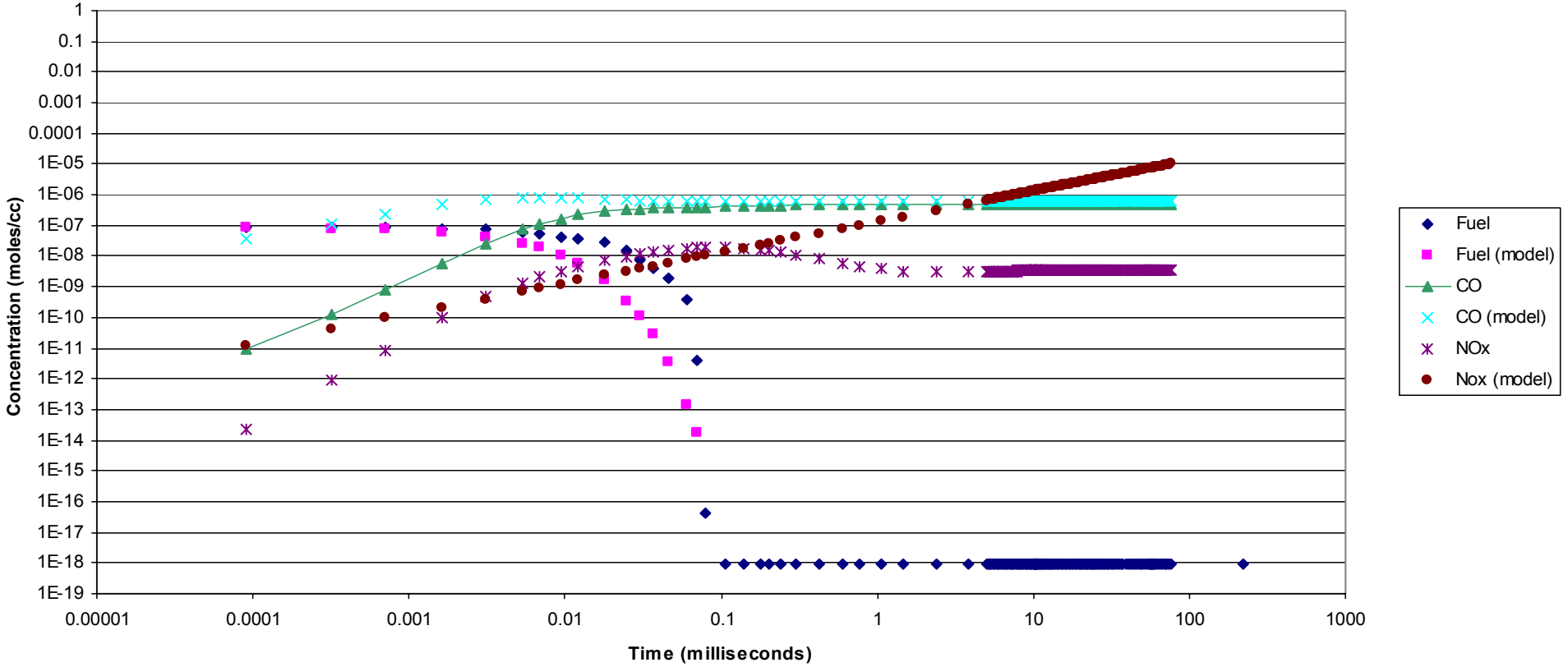


Figure 20
autoignition Jet-a tau*P vs 1/T

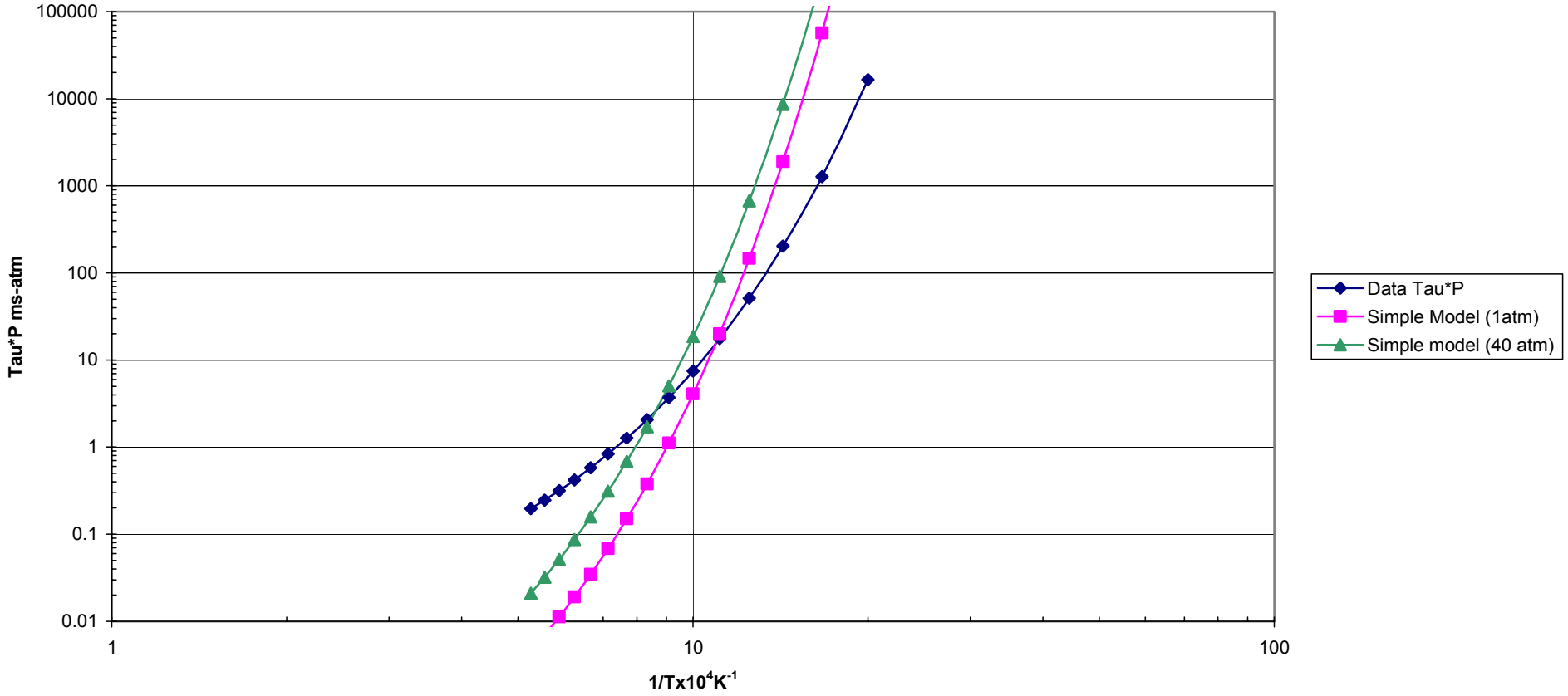


Figure 21
COeq Correlation
Methane
f/a ≥ 0.068
$Coeq=1.11e^{-2}(f/a)^{3.90}(P)^{0.964}[\exp(-1235/T)]$

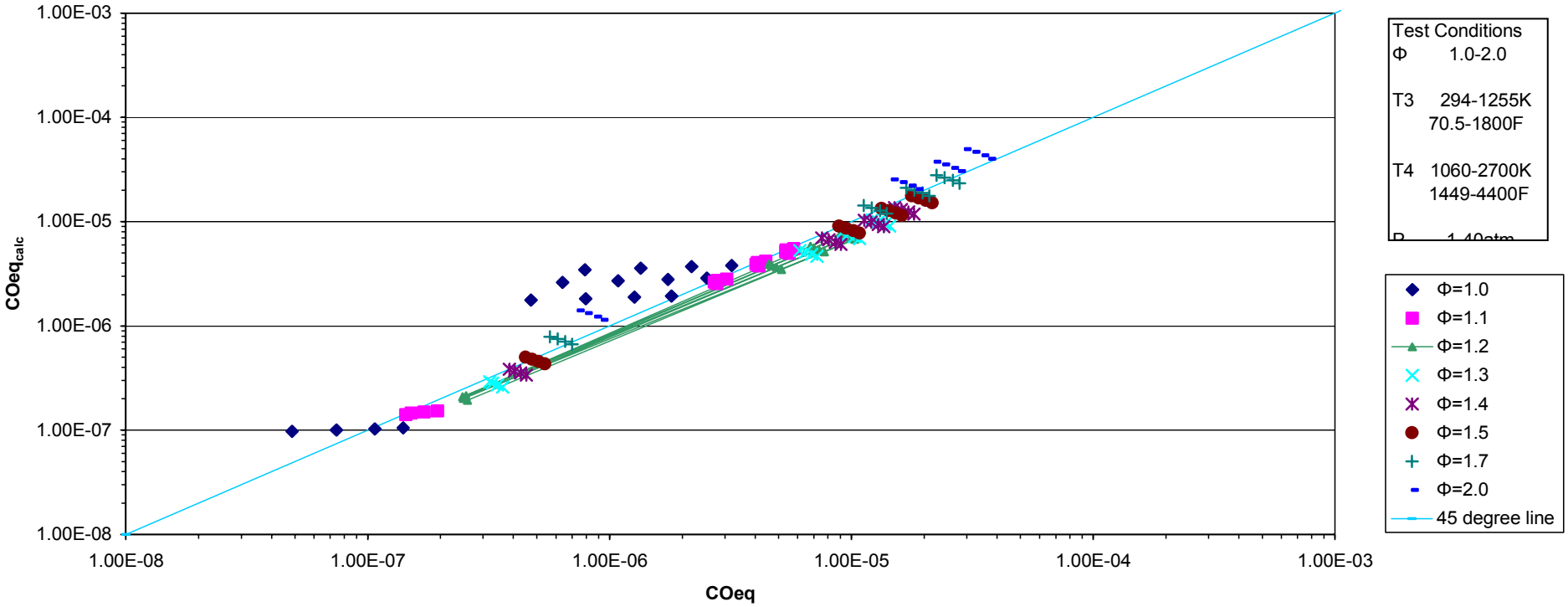


Figure 22
COeq Correlation
Methane
f/a < 0.068
$Coeq=4.98(f/a)^{1.74}(P)^{0.512}[\exp(-31797/T)]$

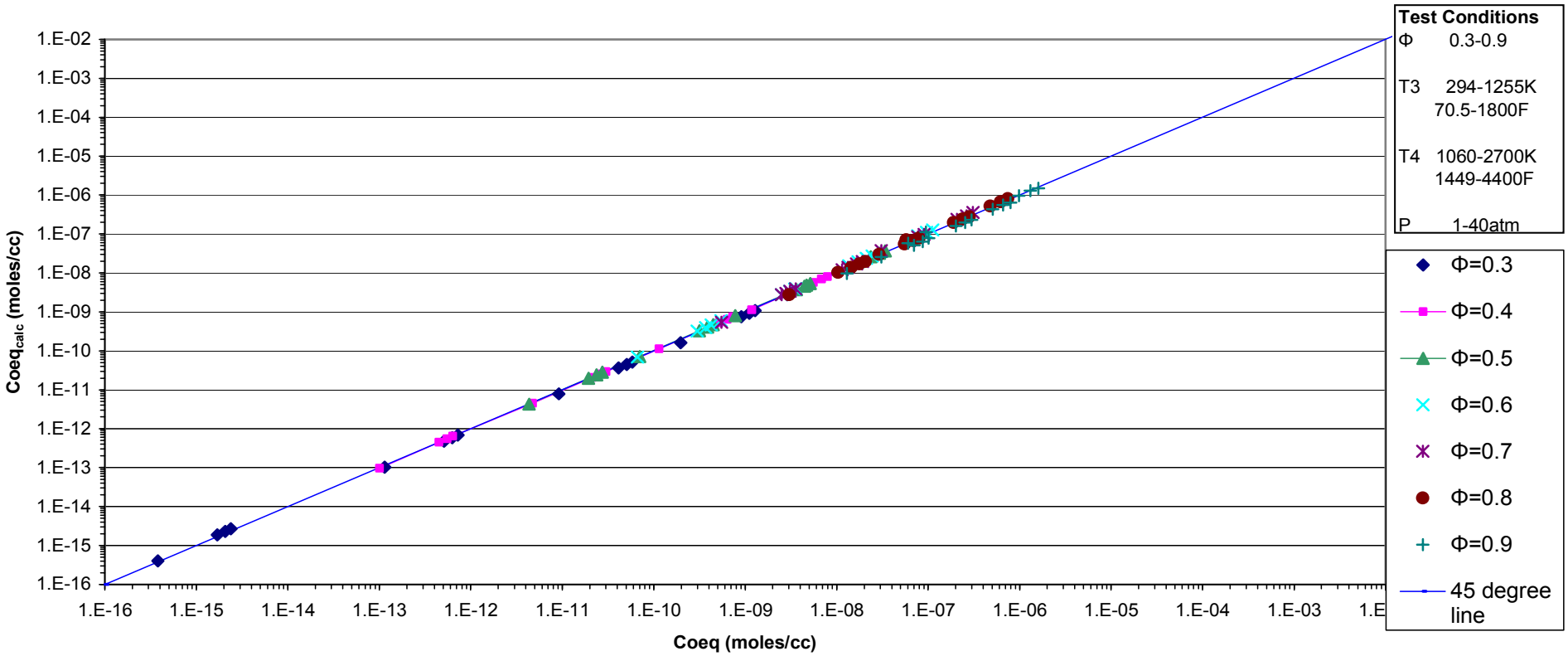


Figure 23
CH4 Fuel Tau Parity
(lean 7/31 cut off data)

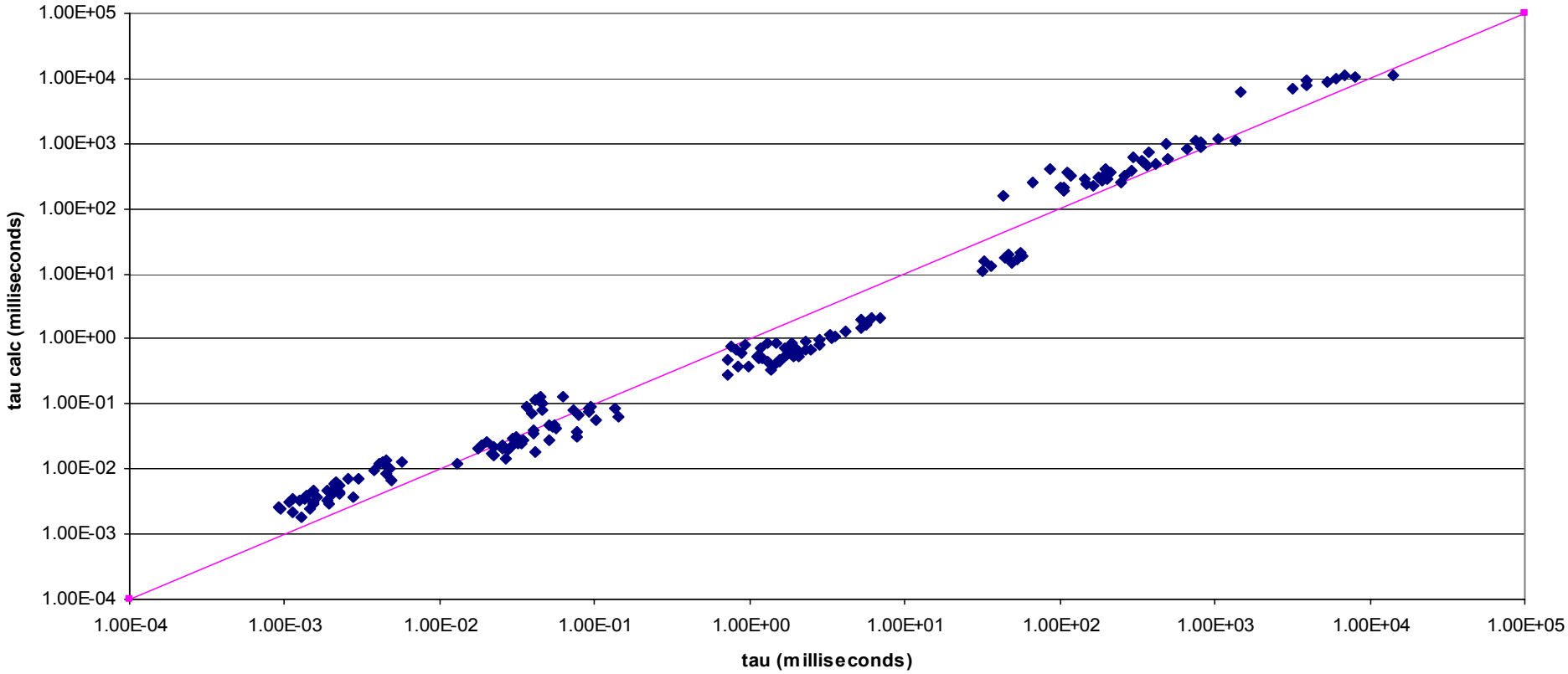


Figure 24
CH4 Fuel Tau Parity
(rich, 7/31,cutoff data)

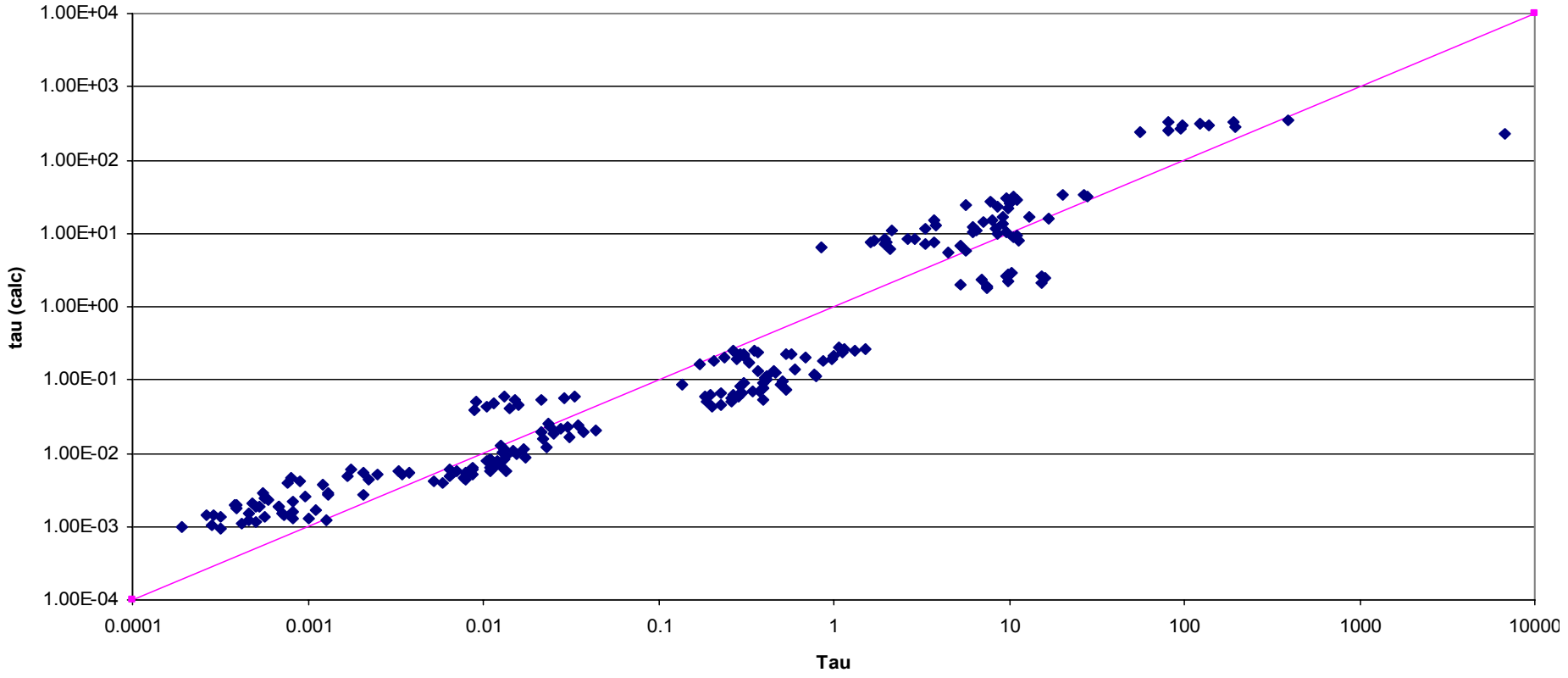


Figure 25
CH4 CO Tau Parity
(lean 7/28 CO2 rates)

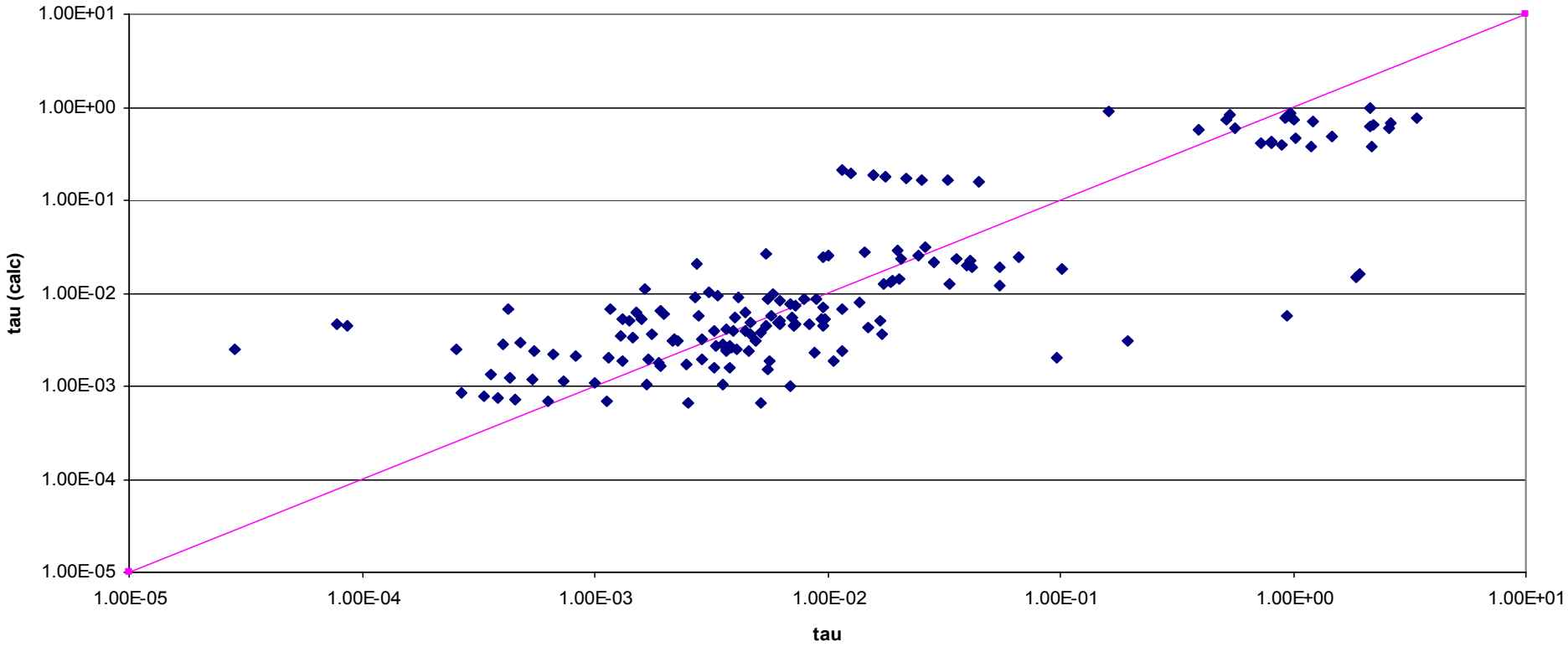


Figure 26
CH4 CO Tau Parity
(rich, 7/31, CO2 rates)

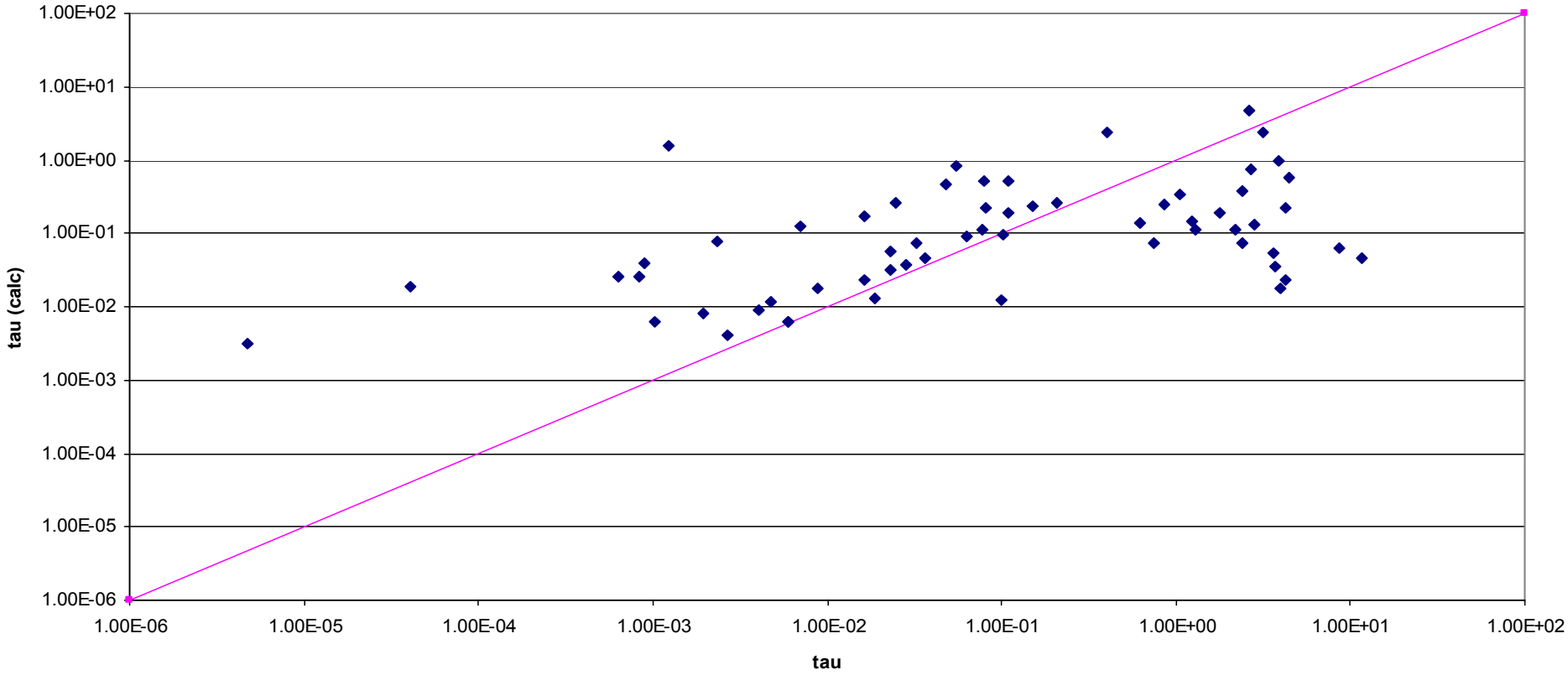


Figure 27
CH4 NOx Tau Parity
(lean 7/31)

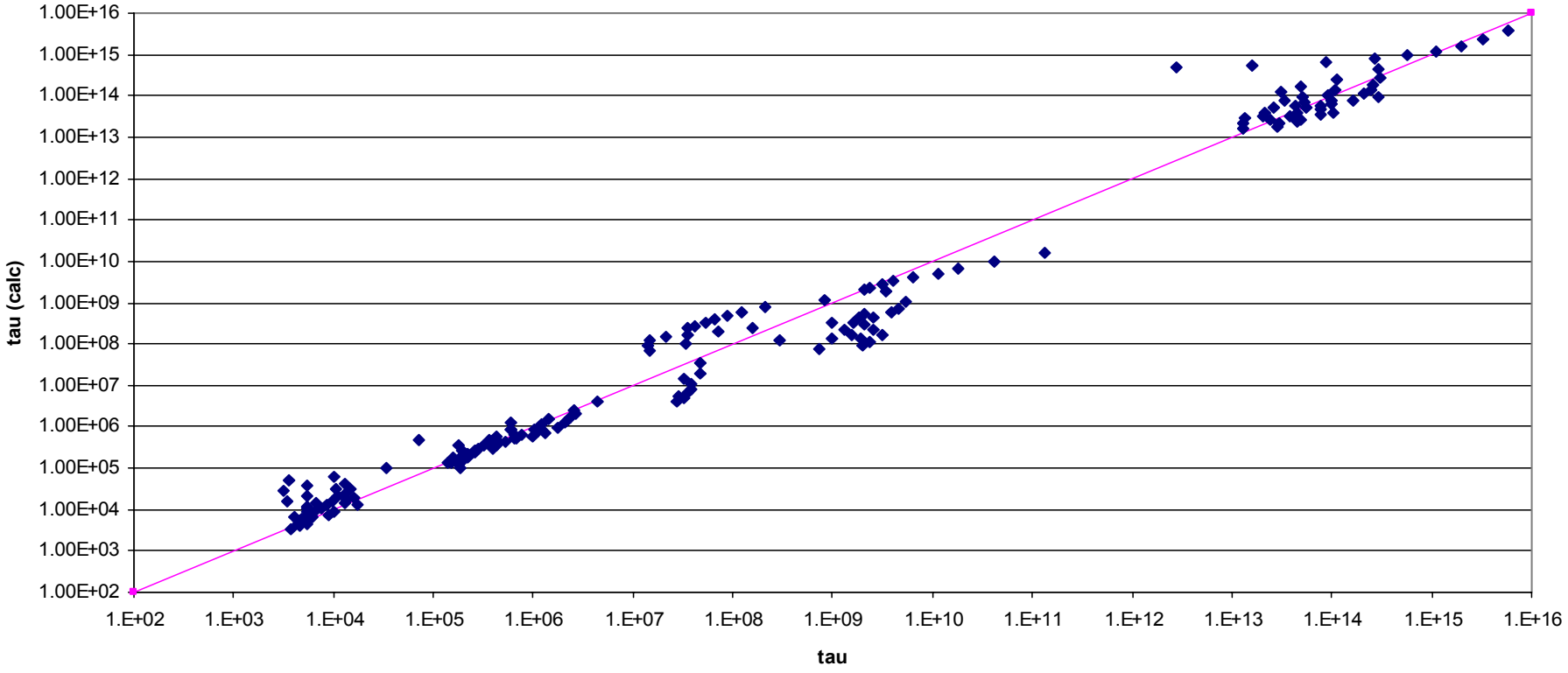
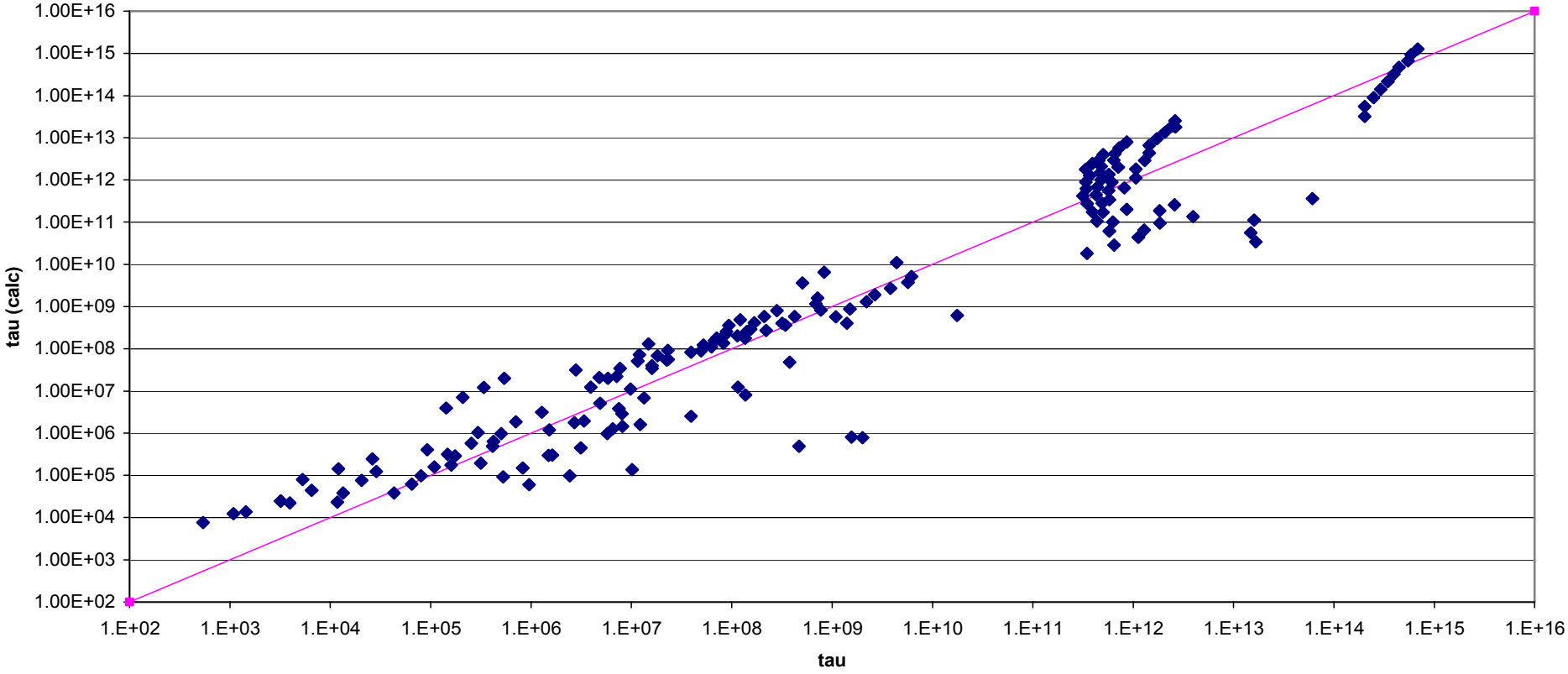


Figure28
CH4 NOx Tau Parity
(rich 7/31)



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Melissa Molnar, Ohio University, Department of Chemical Engineering, Athens, Ohio 45701 and Summer Intern at Ohio Aerospace Institute; and C. John Marek, NASA Glenn Research Center. Responsible person, C. John Marek, organization code 5830, 216–433–3584.

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13. ABSTRACT ***(Maximum 200 words)***

Simplified kinetic schemes for Jet-A and methane fuels were developed to be used in numerical combustion codes, such as the National Combustor Code (NCC) that is being developed at Glenn. These kinetic schemes presented here result in a correlation that gives the chemical kinetic time as a function of initial overall cell fuel/air ratio, pressure, and temperature. The correlations would then be used with the turbulent mixing times to determine the limiting properties and progress of the reaction. A similar correlation was also developed using data from NASA's Chemical Equilibrium Applications (CEA) code to determine the equilibrium concentration of carbon monoxide as a function of fuel air ratio, pressure, and temperature. The NASA Glenn GLSENS kinetics code calculates the reaction rates and rate constants for each species in a kinetic scheme for finite kinetic rates. These reaction rates and the values obtained from the equilibrium correlations were then used to calculate the necessary chemical kinetic times. Chemical kinetic time equations for fuel, carbon monoxide, and NOx were obtained for both Jet-A fuel and methane.

14. SUBJECT TERMS

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