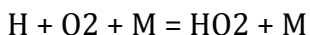


Types of reactions

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Contact info for Max Plomer
email: maxplomer@gmail.com
cell: 203-945-8606

Third body reactions

have a +M in their reaction, they appear in the mechanism file like this:



There is also third body efficiencies that are often listed below the reaction like this:

H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/

Any efficiency not listed is assumed to equal 1

The rate-of-progress variable becomes

$$q_i = \left(\sum_{j=1}^{KK} \alpha_{j,i} c_j \right) \left(k_{f,i} \prod_{j=1}^{KK} c_j^{v_{ji}'} - k_{b,i} \prod_{j=1}^{KK} c_j^{v_{ji}''} \right)$$

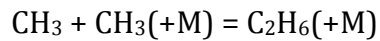
The important concept here is that if all third body efficiencies are 1, then the $\sum_{j=1}^{KK} \alpha_{j,i} c_j$ term just equals the total molar concentration of the mixture.

Duplicate reactions

In chemkin duplicate reactions are supposed to be ignored, unless you write DUPLICATE below the reaction. I currently am ignoring this feature, I read in the DUPLICATE tag but do nothing with it.

Pressure Dependent reactions

They appear very similar to Third body reactions except that they have parentheses around the +M like so:



But an importance distinction is at low pressure (molar concentration low) this will act as the above third body reaction type.

There is always an extra set of Arrhenius coefficients below the reaction, like so:

LOW / 1.040E+26 -2.760 1600.00/

These are for the low pressure limit reaction, and the Arrhenius coefficient that are in the same line as the reaction are used for the high pressure limit

$$k_{low}(T) = A_{low} * \left(\frac{T}{T_0}\right)^{B_{low}} \exp\left(\frac{E_{A,low}}{R_u T}\right)$$

$$k_{high}(T) = A_{high} * \left(\frac{T}{T_0}\right)^{B_{high}} \exp\left(\frac{E_{A,high}}{R_u T}\right)$$

Then the actual forward reaction rate becomes

$$k_f = k_{high} \left(\frac{P_r}{1 + P_r}\right) F$$

P_r is the reduced pressure given by

$$P_r = \frac{k_{low}[M]}{k_{high}}$$

If $F=1$ then this is the Lindemann form, but F can equal other things, in the Troe form F is equal to

$$\log_{10}(F) = \left[1 + \left[\frac{\log_{10}(P_r) + c}{n - d * (\log_{10}(P_r) + c)}\right]^2\right]^{-1} \log_{10}(F_{cent})$$

$$c = -0.4 - 0.67 * \log_{10}(F_{cent})$$

$$n = 0.75 - 1.27 * \log_{10}(F_{cent})$$

$$d = 0.14$$

$$F_{cent} = (1 - \alpha) \exp\left(\frac{-T}{T^{***}}\right) + \alpha \exp\left(\frac{-T}{T^*}\right) + \exp\left(\frac{-T^{**}}{T}\right)$$

The four parameters $\alpha, T^{***}, T^*, T^{**}$ are specified in the mechanism file in this order, often T^{**} is not used and my code can handle both 3 or 4 input parameters. They appear in the mechanism file below the reaction like so:

TROE/ .7830 74.00 2941.00 6964.00 /

A final note here is that Troe/Lindeman forms are just to calculate the forward reaction rate, and you still use the equilibrium constant just like normal to calculate

the reverse reaction rate. Also you do not again use the third body coefficients that were used in Pr term. (There could be a confusion that you multiple the forward reaction rate after being calculated by the thirdbody concentration, but you don't the thirdbody concentration was used in the Pr term)

Other limitations in my code

I am currently only reading 4 elements per molecule, but the current chemkin standard is 5.

Also there are some reactions that do not use equilibrium constant for the reverse reaction, but instead give additional arrehnius coefficients for a reverse reaction. I cannot currently handle these reactions, but you can easily change this type into 2 forward-only reactions. An example mechanism is found here:

<http://lcg.princeton.edu/research/chemical-kinetic-mechanisms/reduced-mechanism-for-iso-octane-oxidation.aspx>

An example of this type of reaction looks like this:

```
ch4+h=ch3+h2      1.73E+04      3      8224
      rev/  6.61E+02      3      7744  /
```

Also my reactor type is specifically design to run fuel and oxidant with a dilutant, there is an automated part that calculates the amount of oxygen you need based on the mixture of fuel species. You might have a completely different type of reaction, in that case there should be no issue, but you would have to remove or modify that code in the reactor that calculated the amount of oxidant based on your problem.

For the octave and octave-fortran hybrid versions, you have to remove all blank lines from chem.inp (also all info must be in chem.inp, no use of a separate file for therm.dat). Also all thermo data must be included, chemkin has a thermo database that it can refer to if you don't include something, I don't have that.

Also I noticed there is some numerical error when analyzing the species mass fractions in the octave-fortran hybrid version, but they disappear when you decrease the ATOL and RTOL values. This may require more timesteps though. Also the octave-fortran hybrid and probably pure octave versions miss out on the highest part of the sharp peak of intermediate species such as H radical due to the linear timestep method, where as the pure matlab solvers are adaptive and add more points at important times.

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