Simplifying the Kinetics for CHEMCAD

CHEMCAD only has several ways you can input kinetics into the kinetic reactor. The "standard form" is the easiest. Note that this reads "Standard – all reactions" in the reactor window. To use this, we must convert the given kinetics equation from the handout into the standard form. The starting equation is:

$$-r_{CO} = \frac{k \cdot T_1 \cdot P_{H_2} \cdot P_{CO}}{\left(1 + k_2 \cdot T_2 \cdot P_{CO}\right)^2}$$

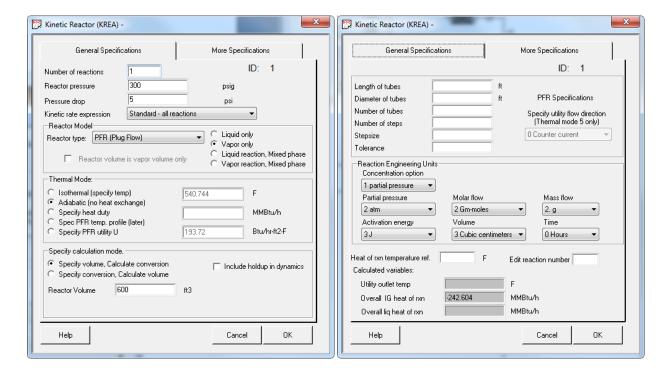
Let's assume that $k_2 \cdot T_2 \cdot P_{CO} >> 1$. Then with this assumption, the equation above reduces to:

$$-r_{\text{CO}} \approx \frac{k \cdot T_{1} \cdot P_{\text{H}_{2}} \cdot P_{\text{CO}}}{\left(k_{2} \cdot T_{2} \cdot P_{\text{CO}}\right)^{2}} = \frac{k \cdot T_{1} \cdot P_{\text{H}_{2}} \cdot P_{\text{CO}}}{\left(k_{2} \cdot T_{2} \cdot\right)^{2} P_{\text{CO}}^{-1}} = \frac{k \cdot T_{1}}{\left(k_{2} \cdot T_{2} \cdot\right)^{2}} \cdot P_{\text{H}_{2}} \cdot P_{\text{CO}}^{-1}$$

Note that in the CHEMCAD reactor, we are allowed to use partial pressures, so we are almost there! All we have to do now is get the term involving k, k_2 , T_1 , and T_2 to look like the usual Arrhenius equation:

$$-r_{\text{CO}} = \frac{.0173}{\left(4.512\right)^2} \cdot \frac{\text{Exp}\!\left[-4492 \cdot \!\left(\frac{1}{T} - \frac{1}{473}\right)\right]}{\left(\text{Exp}\!\left[-8237 \cdot \!\left(\frac{1}{T} - \frac{1}{473}\right)\right]\right)^2} \cdot \frac{P_{\text{H}_2}}{P_{\text{CO}}} = 8.47 \times 10^{-15} \cdot \text{Exp}\!\left[+\frac{11982}{T}\right] \cdot \frac{P_{\text{H}_2}}{P_{\text{CO}}}$$

The units of $-r_{CO}$ are $\frac{gmol}{cc \, cat \cdot hour}$, and this needs to be specified in the CHEMCAD reactor windows:



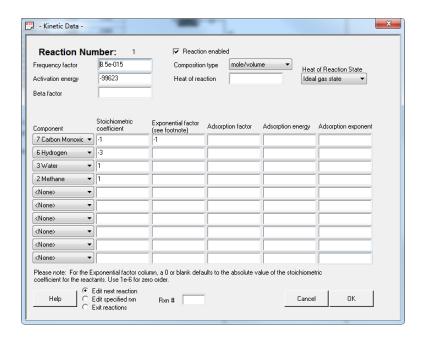
The Arrhenius equation must be specified <u>very carefully</u> in CHEMCAD. The units must be consistent with the CHEMCAD kinetics windows shown above. That is,

$$k = k_0 \cdot e^{-E_a/R \cdot T} = 8.47 \times 10^{-15} \cdot Exp \left[+ \frac{11982}{T} \right] \text{, which means } -\frac{E_a}{R} = 11982$$

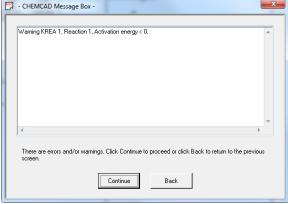
To get the units consistent with the units chosen in CHEMCAD, we must use R = 8.314462 J/gmol-K, giving:

$$E_a = -11982 \cdot 8.314462 \cdot \frac{J}{gmol \cdot K} = -99623 \frac{J}{gmol \cdot K}$$

This is shown in the CHEMCAD kinetics window below:



NOTICE THAT THE ACTIVATION ENERGY IS POSITIVE! CHEMCAD will complain, but it will still work. You will see a message like:



Just click "Continue" and drive on.

One more thing: You should be able to justify the starting assumption that $k_2 \cdot T_2 \cdot P_{\text{CO}} >> 1$.