

## 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:

$$-r_{\text{CO}} = \frac{k \cdot T_1 \cdot P_{\text{H}_2} \cdot P_{\text{CO}}}{(1 + k_2 \cdot T_2 \cdot P_{\text{CO}})^2}$$

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

$$-r_{\text{CO}} \approx \frac{k \cdot T_1 \cdot P_{\text{H}_2} \cdot P_{\text{CO}}}{(k_2 \cdot T_2 \cdot P_{\text{CO}})^2} = \frac{k \cdot T_1 \cdot P_{\text{H}_2} \cdot P_{\text{CO}}}{(k_2 \cdot T_2)^2 P_{\text{CO}}^2} = \frac{k \cdot T_1}{(k_2 \cdot T_2)^2} \cdot P_{\text{H}_2} \cdot P_{\text{CO}}^{-1}$$

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:

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

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

The image displays two screenshots of the Kinetic Reactor (KREA) dialog box in CHEMCAD, showing the configuration for a reactor.

**Left Screenshot (General Specifications):**

- Number of reactions: 1
- Reactor pressure: 300 psig
- Pressure drop: 5 psi
- Kinetic rate expression: Standard - all reactions
- Reactor Model:
  - Reactor type: PFR (Plug Flow)
  - Reactor volume is vapor volume only: ☐
  - Liquid only: ☐
  - Vapor only: ☒
  - Liquid reaction, Mixed phase: ☐
  - Vapor reaction, Mixed phase: ☐
- Thermal Mode:
  - Isothermal (specify temp): 540.744 F
  - Adiabatic (no heat exchange): ☒
  - Specify heat duty: MMBtu/h
  - Spec PFR temp. profile (later): ☐
  - Specify PFR utility U: 193.72 Btu/hr-ft2-F
- Specify calculation mode:
  - Specify volume, Calculate conversion: ☒
  - Specify conversion, Calculate volume: ☐
  - Include holdup in dynamics: ☐
- Reactor Volume: 600 ft3

**Right Screenshot (More Specifications):**

- Length of tubes: ft
- Diameter of tubes: ft
- Number of tubes:
- Number of steps:
- Stepsize:
- Tolerance:
- PFR Specifications:
  - Specify utility flow direction (Thermal mode 5 only): 0 Counter current
- Reaction Engineering Units:
  - Concentration option: 1 partial pressure
  - Partial pressure: 2 atm
  - Molar flow: 2 Gm-moles
  - Mass flow: 2 g
  - Activation energy: 3 J
  - Volume: 3 Cubic centimeters
  - Time: 0 Hours
- Heat of rxn temperature ref.: F
- Edit reaction number:
- Calculated variables:
  - Utility outlet temp: F
  - Overall IG heat of rxn: -242.604 MMBtu/h
  - Overall liq heat of rxn: MMBtu/h

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

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

To get the units consistent with the units chosen in CHEMCAD, we must use  $R = 8.314462 \text{ J/gmol} \cdot \text{K}$ , giving:

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

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  $k_2 \cdot T_2 \cdot P_{CO} \gg 1$ .