

# A First Course on Kinetics and Reaction Engineering

## Example 5.1

### Problem Purpose

This problem illustrates the determination of reaction order and the process for modifying a rate expression so that it displays the proper behavior as the reaction approaches equilibrium.

### Problem Statement

The power-law rate expression in equation (1) was proposed to describe the kinetics of the water-gas shift reaction (2). At 675 K the rate coefficient is equal to  $3.37 \text{ lbmol h}^{-1} \text{ ft}^{-3} \text{ atm}^{-0.55}$  and the equilibrium constant is equal to 12.0.

$$r_2 = k_2 P_{\text{CO}}^{0.9} P_{\text{H}_2\text{O}}^{0.25} P_{\text{CO}_2}^{-0.6} \quad (1)$$



- What is the reaction order with respect to CO and the overall reaction order?
- The expression given in equation (1) will not equal zero when the reaction reaches equilibrium. Modify it so that it will.
- Assuming an initial mixture at 10 atm containing 74% steam, 25% CO and 1% CO<sub>2</sub> and a temperature of 675K, plot the rate from equation (1) and the rate from your answer to part (b) as a function of conversion and comment on the result.

### Problem Solution

(a) In a power law rate expression, the order with respect to a species is just equal to the exponent on that species concentration, or in this case its partial pressure. Hence, the reaction is nine-tenths order in CO. The overall order is just the sum of all the exponents, so in this case the overall reaction order is  $0.9 + 0.25 - 0.6$  or 0.55.

(b) It was mentioned in the informational reading that any expression can be made to display the proper behavior as it approaches equilibrium by multiplying it by the factor given in equation (3). Here we will take the constant  $a$  to equal 1. More generally, the value of the constant  $a$  would have been determined at the same time the reaction orders were determined. Taking  $a$  to equal 1 leads to the rate expression given in equation (4).

$$\left\{ 1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{v_{i,j}}}{K_{eq,j}(T)} \right\}^a \quad (3)$$

$$r_2 = k_2 P_{CO}^{0.9} P_{H_2O}^{0.25} P_{CO_2}^{-0.6} \left\{ 1 - \frac{P_{CO_2} P_{H_2}}{K_2 P_{CO} P_{H_2O}} \right\} \quad (4)$$

(c) We are asked to plot the rates, calculated using equation (1) and separately calculated using equation (4), versus the conversion. However, equations (1) and (4) are not expressed in terms of the conversion; they are expressed in terms of all the species' partial pressures. We are given the initial composition, though, and that can be used along with the CO conversion,  $f_{CO}$ , to calculate all the quantities appearing in equations (1) and (4) for that value of the conversion. First we will assume a basis; I'll use 100 total moles initially. Using the given starting composition, that means that at zero conversion there are 74 moles of water, 25 moles of CO and 1 mole of CO<sub>2</sub>.

By definition, when the CO conversion is equal to  $f_{CO}$ , the moles of CO can be found using equation (5). Again by definition, the extent of reaction can then be found using equation (6), after which the moles of the other species and the total moles can be found using equations (7) through (10). The partial pressures needed in equations (1) and (4) can then be computed using equations (11) through (14), after which the requested rates can be computed using the given values for  $k_2$  and  $K_2$  along with the partial pressures. This can be repeated for several different CO conversions and the results used to construct the requested graph. This is most easily done in a spreadsheet; an Excel spreadsheet that performs these calculations and generates the requested figure accompanies this solution.

$$n_{CO} = n_{CO}^0 (1 - f_{CO}) \quad (5)$$

$$\xi = n_{CO}^0 - n_{CO} \quad (6)$$

$$n_{H_2O} = n_{H_2O}^0 - \xi \quad (7)$$

$$n_{CO_2} = n_{CO_2}^0 + \xi \quad (8)$$

$$n_{H_2} = n_{H_2}^0 + \xi \quad (9)$$

$$n_{total} = n_{CO} + n_{H_2O} + n_{CO_2} + n_{H_2} \quad (10)$$

$$P_{CO} = y_{CO} P_{total} = \frac{n_{CO}}{n_{total}} P_{total} \quad (11)$$

$$P_{H_2O} = \frac{n_{H_2O}}{n_{total}} P_{total} \quad (12)$$

$$P_{CO_2} = \frac{n_{CO_2}}{n_{total}} P_{total} \quad (13)$$

$$P_{H_2} = \frac{n_{H_2}}{n_{total}} P_{total} \quad (14)$$

Following this procedure the values of the rate were computed using equation (1) and equation (4), with the results plotted in Figure 1 below. Rate equation (1) is shown in blue and rate equation (4) in red. If you look at Figure 1, which shows the whole range of conversions, you can see that the two curves are nearly superimposed. Hence, adding the term to account for reversibility doesn't affect the rate at conversions far from equilibrium.

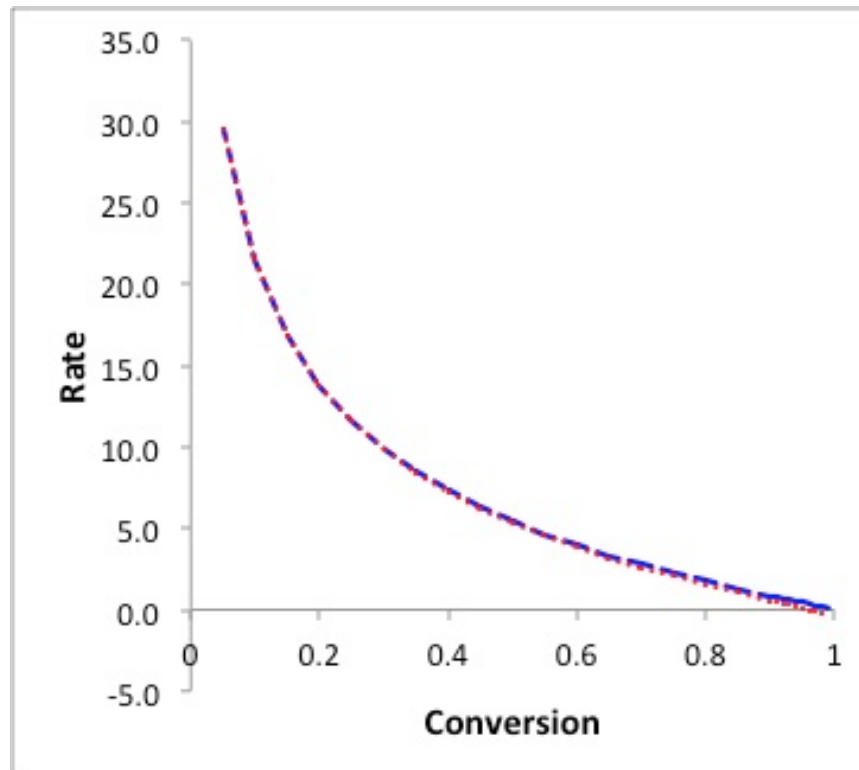


Figure 1. Rate versus conversion calculated using equation (1) (blue) and equation (4) (red).

In Figure 2, however, only the conversions from 90 to 99% are plotted. If you look specifically at 96% conversion (which corresponds to thermodynamic equilibrium at the conditions plotted), you see that rate equation (4) properly predicts the rate to equal zero, whereas rate equation (1) predicts that the reaction is still proceeding. Worse, at conversions greater than equilibrium, rate equation (1) keeps on predicting a positive rate while rate equation (4) correctly predicts that the rate will become negative (that is, the reaction will proceed in the opposite direction if it is beyond equilibrium). If you used rate equation (1) to design a water-gas shift reactor, it would allow you to design a reactor where the conversion went essentially to 100% even though that is impossible!

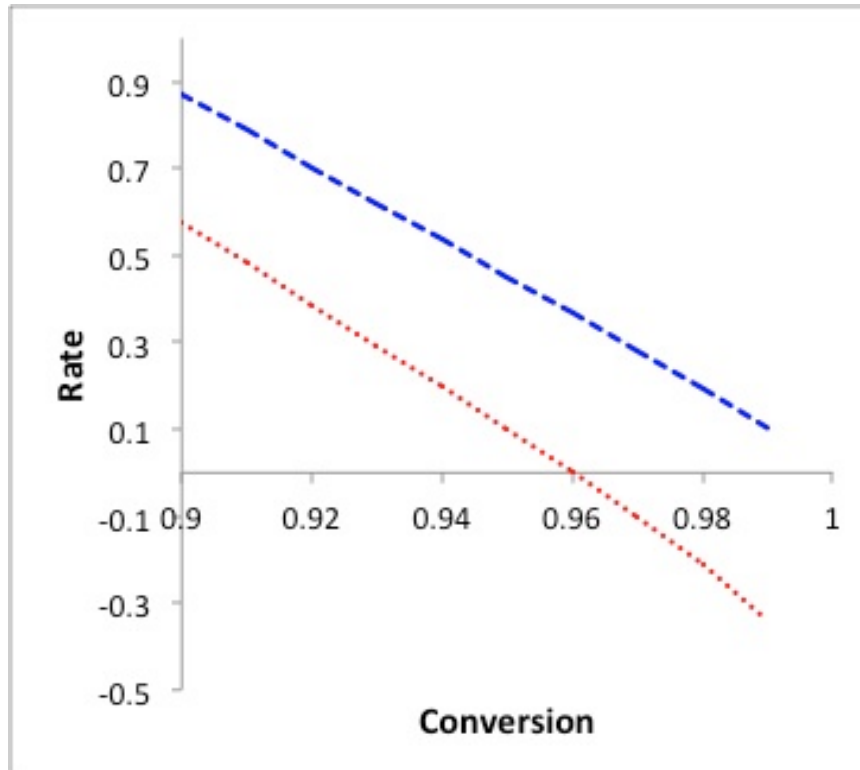


Figure 2. Rate versus conversion calculated using equation (1) (blue) and equation (4) (red) at higher conversions.