REB, The Book
Example 3.6.2 Solution

The water-gas shift, reaction (1), is used commercially to remove CO impurities from hydrogen. Suppose the rate expression shown in equation (2) was validated using experimental data that were far from thermodynamic equilibrium. At 675 K, the rate coefficient, k_1, was found to equal to 3.37 lbmol h^{-1} ft^{-3} $atm^{-0.55}$. In equation (3), that power-law rate expression has been multiplied by a factor that will force it to evaluate to zero at equilibrium. At 675 K, the equilibrium constant, K_1 is equal to 12.0.

If a system initially containing 75% H_2O, 24% CO, and 1% CO_2 at 10 atm and 675 K reacts isothermally and isobarically, the equilibrium conversion of CO will equal 96.3%. The net rate should go to zero at this conversion.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

$$r_1 = k_1 P_{CO}^{0.9} P_{H_2O}^{0.25} P_{CO_2}^{-0.6} \tag{2}$$

$$r_1 = k_1 P_{CO}^{0.9} P_{H_2O}^{0.25} P_{CO_2}^{-0.6} \left\{ 1 - \frac{P_{CO_2} P_{H_2}}{K_1 P_{CO} P_{H_2O}} \right\} \tag{3}$$

For the system described above, make a plot of the net rate of reaction (1) predicted by equations (2) and (3) at CO conversions between 0 and 100%. Then make a second plot at conversions between 85 and 100%. Comment upon the results.

After choosing a basis of one mole initially present, equation (4), the initial molar amounts of the reagents can be calculated, equations (5) through (8).

$$n_{total,0} = 1.0 \text{ mol (basis)} \tag{4}$$

$$n_{CO,0} = y_{CO,0} n_{total,0} = 0.75 \text{ mol} \tag{5}$$

$$n_{H_2O,0} = y_{H_2O,0} n_{total,0} = 0.24 \text{ mol} \tag{6}$$

$$n_{CO_2,0} = y_{CO_2,0} n_{total,0} = 0.01 \text{ mol} \tag{7}$$

$$n_{H_2,0} = y_{H_2,0} n_{total,0} = 0 \text{ mol} \tag{8}$$

Knowing the initial moles of CO, the final moles of CO at any conversion can be calculated using the definition of conversion, equation (9). Knowing that, the extent of reaction can be calculated, equation (10).

$$n_{CO} = n_{CO,0}\left(1 - f_{CO}\right) \tag{9}$$

$$n_{CO} = n_{CO,0} - \xi_1 \quad \Rightarrow \quad \xi_1 = n_{CO,0} - n_{CO} \tag{10}$$

The final molar amounts of the other reagents can next be computed using their initial amounts and the extent of reaction, equations (11) through (13).

$$n_{H_2O} = n_{H_2O,0} - \xi_1 \tag{11}$$

$$n_{CO_2} = n_{CO_2,0} - \xi_1 \tag{12}$$

$$n_{H_2} = \cancel{n_{H_2,0}} + \xi_1 \tag{13}$$

The total number of moles does not changed due to reaction, so the final mole fractions of the reagents equals their final molar amounts divided by the initial total moles. Multiplying the total pressure by the final mole fractions yields the partial pressures of the reagents, equations (14) through (17).

$$P_{CO} = \frac{n_{CO}}{n_{total,0}} P \tag{14}$$

$$P_{H_2O} = \frac{n_{H_2O}}{n_{total,0}} P \tag{15}$$

$$P_{CO_2} = \frac{n_{CO_2}}{n_{total,0}} P \tag{16}$$

$$P_{H_2} = \frac{n_{H_2}}{n_{total,0}} P \tag{17}$$

With those results, the rates predicted by equations (2) and (3) can be calculated for any CO conversion.

Results and Discussion

The calculations were performed as described above. Figure 1 shows the rate of reaction (1) predicted by equations (2) and (3) at conversions between 0 and 100%, based upon isothermal, isobaric reaction of an initial mixture containing 75% H_2O, 24% CO, and 1% CO_2 at 10 atm and 675 K. Figure 2 shows the same data, but only for conversions between 85 and 100%.

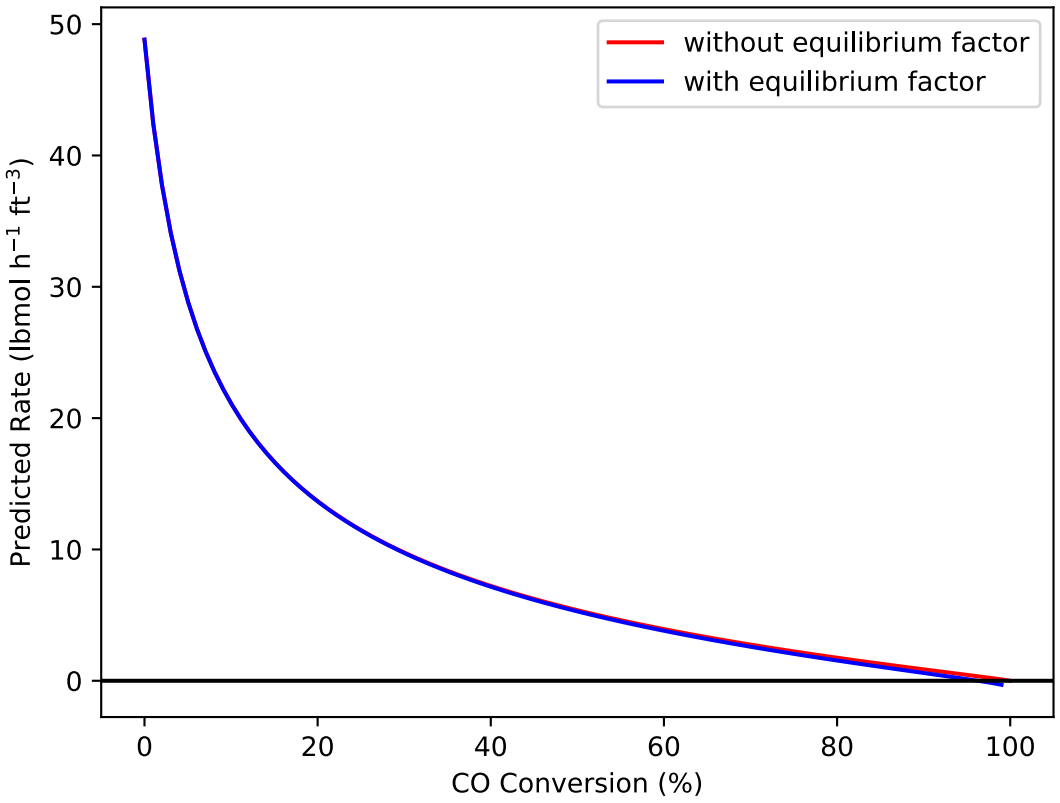

Figure 1. Rate of water-gas shift as a function of CO conversion as predicted by power-law rate expressions with and without a factor that forces them to evaluate to zero at equilibrium.

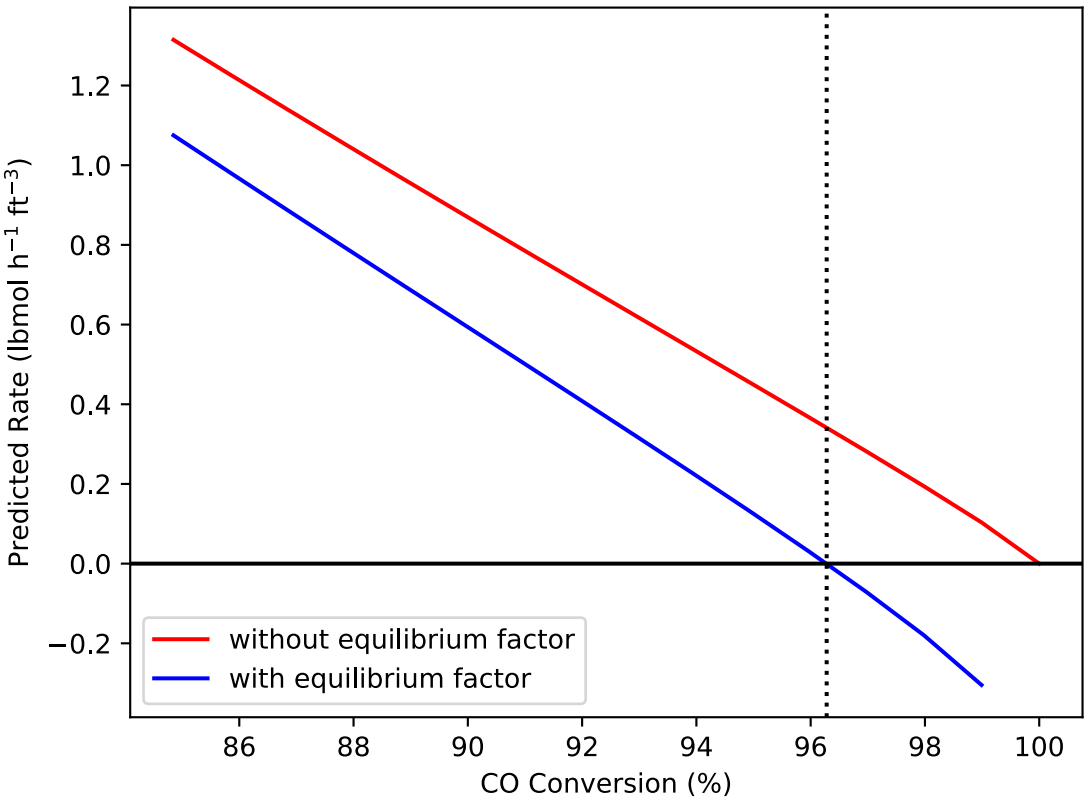

Figure 2. Rate of water-gas shift at conversions near equilibrium as predicted by power-law rate expressions with and without a factor that forces them to evaluate to zero at equilibrium. The dashed line indicates the equilibrium conversion.

The figures allow two important observations. First, Figure 1 shows that adding the term to force proper behavior at equilibrium does not affect the predicted rate at conditions far from equilibrium. Hence, since rate expression (2) was validated and found to be accurate at conditions far from equilibrium, the figure shows that rate expression (3) will be equally accurate at those conditions.

Second, Figure 2 shows that when the reaction reaches equilibrium at 96.3% conversion (dashed line in the figure), rate expression (2) predicts that the net rate will equal 0.37 lbmol h^{-1} ft^{-3} while rate expression (3) correctly predicts the rate will be zero. The consequences of using rate expression (2), for example to design a reactor where

the conversion approaches equilibrium, could be severe. The design calculations would indicate that, for example, 98% conversion could be achieved in the reactor, but of course, if the reactor was built, the conversion would never exceed 96.3%. If rate expression (3) was used to design a reactor, the calculations would indicate that the largest possible conversion is 96.3%.