A First Course on Kinetics and Reaction Engineering

Example 4.3

Problem Purpose

This example illustrates possible consequences of using a rate expression that does not display the proper mathematical behavior.

Problem Statement

A newly hired engineer was asked to design a reactor where reaction (1) would take place. The reactor is to be used to generate methanol from a mixture with a composition of 25% CO, 25% CO_2 and 50% H_2. It was to operate at 0.5 MPa and 550 K, and the amount of methanol needed per hour was specified. The engineer found a study where the rate expression shown below as equation (2) was said to apply for reaction (1). The study gave values for the constants appearing in equation (2). The engineer performed a few quick lab experiments to check the expression and found that it did, indeed, predict the same rate as he measured in his experiments. He then used the rate expression and designed a reactor that would operate with a 75% conversion and sized it to produce the required amount of methanol. When the reactor was built, it did not produce the specified amount of methanol. A senior engineer traced the problem to the rate expression. What is wrong with the expression the younger engineer used?

$$CO + 2\ H_2 \rightleftarrows CH_3OH \tag{1}$$

$$r_{CH_3OH,1} = k_0 \exp\left\{-\frac{E}{RT}\right\} P_{CO}\left(P_{total} + \sqrt{P_{H_2}}\right) \tag{2}$$

Problem Solution

There are two criteria that rate expressions should meet: they should be single valued and they should predict that the rate is zero when the environmental variables correspond to equilibrium values. This rate expression fails on both counts. Just by examination it can be seen that the rate will be positive at the initial conditions, and it will remain positive until the partial pressure of CO becomes zero. Example 2 from Unit 3 showed that this reaction is reversible, so its net rate should become zero before all the CO is consumed. (Note, even worse, if the feed contained excess CO, this expression would still predict a positive rate after all the hydrogen had been consumed!) It can be shown that the rate expression is double valued by examining the final term in parentheses. The total pressure will always be larger than the partial pressure of hydrogen, and it will always be positive. The partial pressure of hydrogen will always be positive or zero. Hence, the square root will not be imaginary; it will have two roots, one positive and one negative. Since the total pressure is larger than the hydrogen partial pressure, adding either the positive root or the negative root to the total pressure will still give a real positive value for the rate of reaction. Thus, this rate expression will give two different rates for any set of conditions.