A First Course on Kinetics and Reaction Engineering

Example 8.1

Problem Purpose

This problem illustrates the simplification of a mechanistic rate expression for a non-elementary reaction when the associated mechanism includes a rate-determining step.

Problem Statement

At high temperatures nitric oxide can be reduced by molecular hydrogen. Macroscopically, the reaction appears to occur as written in reaction (1). Suppose that the mechanism presented in reactions (2) through (4) is being evaluated to determine whether it is consistent with experimental kinetics. If step (4) is assumed to be rate-determining, what is the rate expression that results?

Overall reaction:

$$2\ NO + 2\ H_2 \rightleftarrows N_2 + 2\ H_2O \tag{1}$$

Proposed mechanism:

$$2\ NO \rightleftarrows N_2O_2 \tag{2}$$

$$H_2 + N_2O_2 \rightleftarrows N_2 + H_2O_2 \tag{3}$$

$$H_2 + H_2O_2 \rightleftarrows 2\ H_2O \tag{4}$$

Problem Analysis

When a mechanism includes a rate-determining step, the rate expression for the corresponding non-elementary reaction can be set equal to the rte of the rate-determining step. If the resulting rate expression contains concentrations of reactive intermediates, they can be eliminated by writing quasi-equilibrium expressions for the other steps and solving them to obtain expressions for the concentrations of the reactive intermediates. The latter can then be substituted into the rate expression.

Problem Solution

We begin by checking that there is a linear combination of the mechanistic steps that adds up to give the overall reaction. We can see by inspection that if we add all three steps together, the result is reaction (1), so the mechanism is consistent with the overall stoichiometry. Next, since step (4) is the rate-determining step (rds), the overall rate is set equal to the forward rate of step (4) leading to the overall rate expression given in equation (5). H_2O_2 and N_2O_2 are reactive intermediates since they appear in the mechanism, but not in the macroscopically observed reaction. Consequently, it is necessary to eliminate the partial pressure of H_2O_2 from equation (5).

$$r_1 = r_{rds} = r_{4,f} = k_4 P_{H_2} P_{H_2O_2} \tag{5}$$

To eliminate the partial pressure of H_2O_2 from equation (5) first notice that all steps other than the rate-determining step, here steps (2) and (3), are then at quasi-equilibrium, so for each of them an equilibrium expression can be written, giving equations (6) and (7).

$$K_2 = \frac{P_{N_2O_2}}{P_{NO}^2} \tag{6}$$

$$K_3 = \frac{P_{N_2}P_{H_2O_2}}{P_{H_2}P_{N_2O_2}} \tag{7}$$

Equations (6) and (7) can be solved to obtain a expressions for the partial pressures of the reactive intermediates, H_2O_2 and N_2O_2, in terms of the equilibrium constants and the partial pressures of stable species. Doing so leads to equations (8) and (9).

$$P_{N_2O_2} = K_2 P_{NO}^2 \tag{8}$$

$$P_{H_2O_2} = \frac{K_2 K_3 P_{NO}^2 P_{H_2}}{P_{N_2}} \tag{9}$$

Equation (9) can be substituted into rate expression (5) for the partial pressure of H_2O_2, producing the desired result as given in equation (10).

$$r_1 = \frac{k_4 K_2 K_3 P_{NO}^2 P_{H_2}^2}{P_{N_2}} \tag{10}$$

Roberts (“Chemical Reactions and Chemical Reactors,” Wiley, 2009.) points out that the mechanism proposed here has some flaws. The first step is unimolecular in the reverse direction, the second requires three bonds to break and three more to form in a single molecular event, and the third requires two bonds to break and two more to form in a single molecular event. For these reasons, the steps in this mechanism are not likely to be elementary. Nonetheless, even mechanisms that are flawed in this way can sometimes provide useful insight into reactions with complex kinetics. In the present example, the final rate expression, equation (10), is not consistent with experimental kinetics studies that show the rate to be proportional to the NO partial pressure squared and the hydrogen partial pressure to the first power.