A First Course on Kinetics and Reaction Engineering

Example 6.2

Problem Purpose

This problem shows how to check the plausibility of a chain reaction mechanism, identify the different types of elementary reaction steps within it and use it to generate a rate expression for the macroscopically observed, non-elementary reaction to which it corresponds.

Problem Statement

Suppose that nitrogen oxidation, equation (1), occurs via the chain reaction mechanism given in equations (2) through (5). Classify each of the mechanistic steps as initiation/termination, propagation, chain branching or chain transfer, show that there is a linear combination of equations (2) through (5) that is equal to equation (1), and write the generalized rate expression for reaction (1) that is predicted by the mechanism.

$$N_2 + O_2 \rightleftarrows 2\,NO \tag{1}$$

$$O_2 \rightleftarrows 2\,O \tag{2}$$

$$O + N_2 \rightleftarrows NO + N \tag{3}$$

$$N + O_2 \rightleftarrows NO + O \tag{4}$$

$$2\,N \rightleftarrows N_2 \tag{5}$$

Problem Analysis

If reaction (1) is equal to a linear combination of reactions (2) through (5), then it is not mathematically independent of them. The rate with respect to a reactant or product is simply the sum of the rate of each step with respect to that species. The generalized rate can then be found by dividing that rate expression by the stoichiometric coefficient of that species.

Problem Solution

The problem statement tells us that reactions (2) through (5) constitute a chain reaction mechanism. The mechanism includes two chemical species, N and O, that are not participants in the macroscopically observed, overall reaction, equation (1). These two species are reactive intermediates. Looking at reaction (2), the reactant is not a reactive intermediate, but the reaction does produce reactive intermediates. Similarly, reaction (5) consumes two reactive intermediates without producing any new ones. Since these reactions are reversible, the can be classified as initiation/termination steps. Reaction (3) consumes an O and produces an N, while reaction (4) does the opposite. Hence, reactions (3) and (4) are propagation steps.

We are next asked whether there is a linear combination of the mechanistic steps that is equal to the macroscopically observed, non-elementary reaction. By definition in a chain reaction, the propagation steps must combine to produce the apparent macroscopic reaction. Adding the propagation steps, reactions (3) and (4), gives equation (6), where it can see that N and O each appear on both sides of the reaction equations and therefore cancel out leading to reaction (1). Thus, there is a linear combination of the mechanistic steps that is equal to the macroscopically observed, non-elementary reaction.

$$O + N_2 + N + O_2 \rightleftarrows NO + N + NO + O \tag{6}$$

Finally, the problem asks for a rate expression for the generalized rate of reaction (1). The rate with respect to NO can be found by substitution of NO for i and 1 for j in equation (7). Since each of the mechanistic steps is elementary by definition, their rate expressions are given by equation (8) where the rate coefficients are typically assumed to obey the Arrhenius expression. Equation (9) results after making the indicated substitutions. A rate expression for the generalized rate of reaction (1) can then be found as shown in equation (10).

$$r_{i,j} = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} r_s \tag{7}$$

$$r_{i,j} = \sum_{\substack{s=\text{ all}\\ \text{steps}}} \nu_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all}\\ \text{reactants}}} \left[m\right]^{-\nu_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all}\\ \text{products}}} \left[n\right]^{\nu_{n,s}} \right) \tag{8}$$

$$r_{NO,1} = k_{3,f}\left[O\right]\left[N_2\right] - k_{3,r}\left[NO\right]\left[N\right] + k_{4,f}\left[N\right]\left[O_2\right] - k_{4,r}\left[NO\right]\left[O\right] \tag{9}$$

$$r_1 = \frac{r_{NO,1}}{\nu_{NO,1}} = \frac{k_{3,f}\left[O\right]\left[N_2\right] - k_{3,r}\left[NO\right]\left[N\right] + k_{4,f}\left[N\right]\left[O_2\right] - k_{4,r}\left[NO\right]\left[O\right]}{2} \tag{10}$$