A First Course on Kinetics and Reaction Engineering

Example 10.2

Problem Purpose

This problem illustrates the derivation of a simple Langmuir-Hinshelwood rate expression. In doing so, it also illustrates the use of fractional coverage as a composition variable and the use of the expression for the conservation of catalytic sites.

Problem Statement

Suppose the macroscopically observed reaction given in equation (1) is catalyzed by a heterogeneous catalyst, and the corresponding reaction mechanism is given by equations (2) through (6). Assume all adsorption processes to be equilibrated and mechanistic step (4) to be rate-determining. Derive a rate expression for the rate of reaction (1).

$$\text{A} + \text{B} \rightarrow \text{C} + \text{D} \tag{1}$$

$$\text{A} + \ast \rightleftarrows \text{A-}\ast \tag{2}$$

$$\text{B} + \ast \rightleftarrows \text{B-}\ast \tag{3}$$

$$\text{A-}\ast + \text{B-}\ast \rightarrow \text{C-}\ast + \text{D-}\ast \tag{4}$$

$$\text{C-}\ast \rightleftarrows \text{C} + \ast \tag{5}$$

$$\text{D-}\ast \rightleftarrows \text{D} + \ast \tag{6}$$

Problem Analysis

This problem asks us to generate a rate expression from a heterogeneous catalytic reaction mechanism. Since step (4) is identified as rate-determining, the overall rate will be equal to the rate of this step. Steps (2), (3), (5) and (6) can then be modeled as being quasi equilibrated; in combination with an expression for the conservation of sites, these equations can be used to obtain expressions for the surface coverages. Those expressions can then be substituted into the rate expression, leading to an expression in terms of partial pressures of fluid-phase species and constants.

Problem Solution

Since step (4) is rate-determining, the rate of the apparent reaction, equation (1), will equal the forward rate of step (4), as expressed in equation (7). This rate expression is of limited utility due to the appearance of surface coverages of A and B. These quantities are difficult to measure, and it is preferred to eliminate them from the rate expression.

$$r_1 = r_{4,f} = k_{4,f}\theta_A\theta_B \tag{7}$$

Because step (4) is rate-determining, the other steps in the mechanism, reactions (2), (3), (5) and (6), may be assumed to be quasi-equilibrated. Corresponding equilibrium expressions are given in equations (8) through (11). (Note, the latter two equilibrium expressions were written as adsorption equilibria, that is, the equilibrium constants, K_5 and K_6, are for the reverse of reactions (5) and (6), as they appear in the mechanism.) Equations (8) through (11) contain five fractional coverages (θ_v, θ_A, θ_B, θ_C and θ_D), but there are only four equations. The fifth equation that we need is the conservation of active sites, equation (12). Applying this equation to the present problem gives equation (13).

$$K_2 = \frac{\theta_A}{P_A \theta_v} \tag{8}$$

$$K_3 = \frac{\theta_B}{P_B \theta_v} \tag{9}$$

$$K_5 = \frac{\theta_C}{P_C \theta_v} \tag{10}$$

$$K_6 = \frac{\theta_D}{P_D \theta_v} \tag{11}$$

$$\theta_v + \sum_{\substack{i = \text{all} \\ \text{adsorbed} \\ \text{species}}} \theta_i = 1 \tag{12}$$

$$\theta_v + \theta_A + \theta_B + \theta_C + \theta_D = 1 \tag{13}$$

Equations (8), (9), (10), (11), and (13) can be solved to obtain expressions for the fractional coverages of the five surface species. This can be performed manually or using symbolic algebra software. In either case, the results are given in equations (14) through (18).

$$\theta_v = \frac{1}{1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D} \tag{14}$$

$$\theta_A = \frac{K_2 P_A}{1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D} \tag{15}$$

$$\theta_B = \frac{K_3 P_B}{1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D} \tag{16}$$

$$\theta_C = \frac{K_5 P_C}{1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D} \tag{17}$$

$$\theta_D = \frac{K_6 P_D}{1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D} \tag{18}$$

Substitution of equations (15) and (16) into equation (7) gives the desired rate expression in terms of only fluid-phase partial pressures and constants, equation (19).

$$r_1 = r_{4,f} = \frac{k_{4,f} K_2 K_3 P_A P_B}{\left(1 + K_2 P_A + K_3 P_B + K_5 P_C + K_6 P_D\right)^2} \tag{19}$$