REB, The ?
[Assignment ID] Solution

Suppose the non-elementary reaction (1) is heterogeneously catalyzed, and the corresponding reaction mechanism is given by equations (2) through (6). Assume step (4) is rate-determining and derive an expression for the apparent rate of reaction (1) that does not include fractional coverages.

$$A + B \rightleftarrows Y + Z \qquad (1)$$

$$A + \ast \rightleftarrows A\text{–}\ast \qquad (2)$$

$$B + \ast \rightleftarrows B\text{–}\ast \qquad (3)$$

$$A\text{–}\ast + B\text{–}\ast \rightarrow Y\text{–}\ast + Z\text{–}\ast \qquad \text{(rate det.) } (4)$$

$$Y\text{–}\ast \rightleftarrows Y + \ast \qquad (5)$$

$$Z\text{–}\ast \rightleftarrows Z + \ast \qquad (6)$$

Assignment Summary

<u>Apparent Reaction</u>:

$$A + B \rightleftarrows Y + Z \qquad (1)$$

<u>Mechanistic Steps</u>:

$$A + \ast \rightleftarrows A\text{–}\ast \qquad (2)$$

$$B + \ast \rightleftarrows B\text{–}\ast \qquad (3)$$

$$A\text{–}\ast + B\text{–}\ast \rightarrow Y\text{–}\ast + Z\text{–}\ast \qquad \text{(rate det.) } (4)$$

$$Y\text{–}\ast \rightleftarrows Y + \ast \qquad (5)$$

$$Z\text{–}\ast \rightleftarrows Z + \ast \qquad (6)$$

<u>Quantifiable Reagents</u>: A, B, Y, and Z

Reactive Intermediates: ✳, A–✳, B–✳, Y–✳, Z–✳

Deliverables: simplified expression for r_1

Equations for Generating the Mechanistic Rate Expression

Apparent Rate of the Non-Elementary Reaction

$$r_1 = r_4 = k_{4,f}\theta_A\theta_B - k_{4,r}\theta_Y\theta_Z \tag{7}$$

Quasi-Equilibrium Expressions

$$K_2 = \frac{\theta_A}{\left[A\right]\theta_v} \tag{8}$$

$$K_3 = \frac{\theta_B}{[B]\,\theta_v} \tag{9}$$

$$K_5 = \frac{[Y]\,\theta_v}{\theta_Y} \tag{10}$$

$$K_6 = \frac{[Z]\,\theta_v}{\theta_Z} \tag{11}$$

Site Conservation Equation

$$1 = \theta_v + \theta_A + \theta_B + \theta_Y + \theta_Z \tag{12}$$

Calculations

The algebraic details for the calculations in this section are presented in the file, Example 4.8.5 Calculations.pdf. The calculations proceed as follows:

1. Solve equations (8) through (12) to get expressions for the fractional conversions.

$$\theta_v = \frac{1}{1 + K_2\left[A\right] + K_3[B] + \frac{1}{K_5}[Y] + \frac{1}{K_6}[Z]} \tag{13}$$

$$\theta_A = \frac{K_2 \left[A\right]}{1 + K_2 \left[A\right] + K_3 \left[B\right] + \frac{1}{K_5} \left[Y\right] + \frac{1}{K_6} \left[Z\right]} \tag{14}$$

$$\theta_B = \frac{K_3 \left[B\right]}{1 + K_2 \left[A\right] + K_3 \left[B\right] + \frac{1}{K_5} \left[Y\right] + \frac{1}{K_6} \left[Z\right]} \tag{15}$$

$$\theta_Y = \frac{\frac{1}{K_5} \left[C\right]}{1 + K_2 \left[A\right] + K_3 \left[B\right] + \frac{1}{K_5} \left[Y\right] + \frac{1}{K_6} \left[Z\right]} \tag{16}$$

$$\theta_Z = \frac{\frac{1}{K_6} \left[D\right]}{1 + K_2 \left[A\right] + K_3 \left[B\right] + \frac{1}{K_5} \left[Y\right] + \frac{1}{K_6} \left[Z\right]} \tag{17}$$

2. Substitute equations (14) through (17) into equation (7)

$$r_1 = \frac{k_{4,f} K_2 K_3 \left[A\right] \left[B\right] - \frac{k_{4,r}}{K_5 K_6} \left[Y\right] \left[Z\right]}{\left(1 + K_2 \left[A\right] + K_3 \left[B\right] + \frac{1}{K_5} \left[Y\right] + \frac{1}{K_6} \left[Z\right]\right)^2} \tag{18}$$

Simplification and Discussion

It is convenient to define effective rate coefficients and equilibrium constants as shown in equations (19) through (24), leading to the form of the rate expression shown in equation (25).

$$k'_f = k_{4,f} K_2 K_3 \tag{19}$$

$$k'_r = \frac{k_{4,r}}{K_5 K_6} \tag{20}$$

$$K_A = K_2 \tag{21}$$

$$K_B = K_3 \tag{22}$$

$$K_C = \frac{1}{K_5} \tag{23}$$

$$K_D = \frac{1}{K_6} \tag{24}$$

$$r_1 = \frac{k_f' \left[A\right] \left[B\right] - k_r' \left[C\right] \left[D\right]}{\left(1 + K_A \left[A\right] + K_B \left[B\right] + K_C \left[C\right] + K_D \left[D\right]\right)^2} \tag{25}$$

Assuming the equilibrium constants display Arrhenius temperature dependence, the apparent rate coefficients and equilibrium constants in equation (25) will do so also. A variety of limiting forms are possible when one or more terms in the denominator are negligible relative to the others.

Deliverables

If the mechanism is correct as described, the rate expression has the Langmuir-Hinshelwood form shown below. Experimental studies will need to be performed to determine whether it or any of its limiting forms capture the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = \frac{k_f' \left[A\right] \left[B\right] - k_r' \left[C\right] \left[D\right]}{\left(1 + K_A \left[A\right] + K_B \left[B\right] + K_C \left[C\right] + K_D \left[D\right]\right)^2}$$