# REB, The Course
# Example 4.8.6 Solution

The oxidation of carbon monoxide, reaction (1) is heterogeneously catalyzed. A proposed reaction mechanism is shown in reactions (2) through (6). Assume that step (6) is rate-limiting and derive an expression for the apparent rate of reaction (1) that contains only partial pressures, rate coefficients and equilibrium constants. How does the apparent rate expression change if O–✳ is the most abundant surface intermediate?

Apparent (non-elementary) Reaction

$2\ CO + O_2 \rightleftarrows 2\ CO_2$ (1)

Mechanism

$O_2 + ✳ \rightleftarrows O_2–✳$ (2)

$CO + O_2–✳ \rightleftarrows CO_3–✳$ (3)

$CO_3–✳ \rightleftarrows CO_2 + O–✳$ (4)

$CO + O–✳ \rightleftarrows CO_2–✳$ (5)

$CO_2–✳ \rightleftarrows CO_2 + ✳$ (6)

***Assignment Summary***

Apparent Reaction:

$2\ CO + O_2 \rightleftarrows 2\ CO_2$ (1)

Mechanistic Steps:

$O_2 + ✳ \rightleftarrows O_2–✳$ (2)

$CO + O_2–✳ \rightleftarrows CO_3–✳$ (3)

$CO_3–✳ \rightleftarrows CO_2 + O–✳$ (4)

$CO + O–* \rightleftarrows CO_2–*$ (5)

$CO_2–* \rightleftarrows CO_2 + *$ (rate det) (6)

Quantifiable Reagents: CO, $O_2$, and $CO_2$

Reactive Intermediates: *, $O_2–*$, $CO_3–*$, $CO_2–*$**,** and $O–*$

Deliverable: simplified expression for $r_1$ when $O–*$ is and is not the most abundant intermediate.

### *Equations for Generating the Mechanistic Rate Expression*

Apparent Rate of the Non-Elementary Reaction

$$r_1 = k_{6,f}\theta_{CO_2} - k_{6,r}\left[CO_2\right]\theta_v \quad (7)$$

Quasi-Equilibrium Expressions

$$K_2 = \frac{\theta_{O_2}}{\left[O_2\right]\theta_v} \quad (8)$$

$$K_3 = \frac{\theta_{CO_3}}{\left[CO\right]\theta_{O_2}} \quad (9)$$

$$K_4 = \frac{\left[CO_2\right]\theta_O}{\theta_{CO_3}} \quad (10)$$

$$K_5 = \frac{\theta_{CO_2}}{\left[CO\right]\theta_O} \quad (11)$$

Site Conservation Equation

$$1 = \theta_v + \theta_{O_2} + \theta_{CO_3} + \theta_O + \theta_{CO_2} \quad (12)$$

### *Calculations*

The algebraic details for the calculations in this section are presented in the file, Example 4.8.6 Calculations.pdf. The calculations proceed as follows:

1. Solve equations (8) through (12) for the surface coverages.

$$\theta_v = \frac{1}{\left( \begin{array}{c} 1 + K_2 \left[O_2\right] + K_2 K_3 \left[CO\right] \left[O_2\right] \\ + \frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array} \right)} \tag{13}$$

$$\theta_{O_2} = \frac{K_2 \left[O_2\right]}{\left( \begin{array}{c} 1 + K_2 \left[O_2\right] + K_2 K_3 \left[CO\right] \left[O_2\right] \\ + \frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array} \right)} \tag{14}$$

$$\theta_{CO_3} = \frac{K_2 K_3 \left[CO\right] \left[O_2\right]}{\left( \begin{array}{c} 1 + K_2 \left[O_2\right] + K_2 K_3 \left[CO\right] \left[O_2\right] \\ + \frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array} \right)} \tag{15}$$

$$\theta_O = \frac{\frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]}}{\left( \begin{array}{c} 1 + K_2 \left[O_2\right] + K_2 K_3 \left[CO\right] \left[O_2\right] \\ + \frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array} \right)} \tag{16}$$

$$\theta_{CO_2} = \frac{\frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]}}{\left( \begin{array}{c} 1 + K_2 [O_2] + K_2 K_3 [CO] [O_2] \\ + \frac{K_2 K_3 K_4 [CO] [O_2]}{[CO_2]} + \frac{K_2 K_3 K_4 K_5 [CO]^2 [O_2]}{[CO_2]} \end{array} \right)} \tag{17}$$

2. Substitute equations (13) and (17) into equation (7).

$$r_1 = \frac{k_{6,f} K_2 K_3 K_4 K_5 [CO]^2 [O_2] - k_{6,r} [CO_2]^2}{\left( \begin{array}{c} [CO_2] + K_2 [O_2] [CO_2] + K_2 K_3 [CO] [O_2] [CO_2] \\ + K_2 K_3 K_4 [CO] [O_2] + K_2 K_3 K_4 K_5 [CO]^2 [O_2] \end{array} \right)} \tag{18}$$

***Simplification and Discussion***

Apparent rate coefficients and equilibrium constants can be defined as shown in equations (19) through (24), in which case the rate expression takes the form shown in equation (25).

$$k_f' = k_{6,f} K_2 K_3 K_4 K_5 \tag{19}$$

$$k_r' = k_{6,r} \tag{20}$$

$$K' = K_2 \tag{21}$$

$$K'' = K_2 K_3 \tag{22}$$

$$K''' = K_2 K_3 K_4 \tag{23}$$

$$K'''' = K_2 K_3 K_4 K_5 \tag{24}$$

$$r_1 = \frac{k_f' \left[CO\right]^2 \left[O_2\right] - k_r' \left[CO_2\right]^2}{\left( \begin{array}{c} \left[CO_2\right] + K' \left[O_2\right] \left[CO_2\right] + K'' \left[CO\right] \left[O_2\right] \left[CO_2\right] \\ + K''' \left[CO\right] \left[O_2\right] + K'''' \left[CO\right]^2 \left[O_2\right] \end{array} \right)} \tag{25}$$

Assuming O–✳ to be the most abundant surface intermediate, it's coverage is much greater than all other coverages.

$$\theta_O \gg \theta_v \tag{26}$$

$$\theta_O \gg \theta_{CO_2} \tag{27}$$

$$\theta_O \gg \theta_{CO_3} \tag{28}$$

$$\theta_O \gg \theta_{O_2} \tag{29}$$

When equations (13) through (17) are substituted into the inequality expressions in equations (26) through (29), simplification leads to the inequalities shown in expressions (30) through (33).

$$K_2 K_3 K_4 \left[CO\right] \left[O_2\right] \gg \left[CO_2\right] \tag{30}$$

$$K_2 K_3 K_4 \left[CO\right] \left[O_2\right] \gg K_2 K_3 K_4 K_5 \left[CO\right]^2 \left[O_2\right] \tag{31}$$

$$K_2 K_3 K_4 \left[CO\right] \left[O_2\right] \gg K_2 K_3 \left[CO\right] \left[O_2\right] \left[CO_2\right] \tag{32}$$

$$K_2 K_3 K_4 \left[CO\right] \left[O_2\right] \gg K_2 \left[O_2\right] \left[CO_2\right] \tag{33}$$

Eliminating the negligible terms leads to the simplified rate expression shown in equation (34).

$$r_1 = \frac{k_{6,f} K_2 K_3 K_4 K_5 \left[CO\right]^2 \left[O_2\right] - k_{6,r} \left[CO_2\right]^2}{\left( \begin{array}{c} \cancel{\left[CO_2\right]} + \cancel{K_2 \left[O_2\right] \left[CO_2\right]} + \cancel{K_2 K_3 \left[CO\right] \left[O_2\right] \left[CO_2\right]} \\ + K_2 K_3 K_4 \left[CO\right] \left[O_2\right] + \cancel{K_2 K_3 K_4 K_5 \left[CO\right]^2 \left[O_2\right]} \end{array} \right)}$$

$$r_1 = \frac{k_{6,f} K_2 K_3 K_4 K_5 \left[CO\right]^2 \left[O_2\right] - k_{6,r} \left[CO_2\right]^2}{K_2 K_3 K_4 \left[CO\right] \left[O_2\right]} \tag{34}$$

However, the rate coefficients and equilibrium constants can be combined as shown in equations (35) and (36), leading to the rate expression shown in equation (37).

$$k_f'' = k_{6,f} K_5 \tag{35}$$

$$k_r'' = \frac{k_{6,r}}{K_2 K_3 K_4} \tag{36}$$

$$r_1 = k_f'' \left[CO\right] - k_r'' \frac{\left[CO_2\right]^2}{\left[CO\right] \left[O_2\right]} \tag{37}$$

If the equilibrium constants for the mechanistic steps display Arrhenius temperature dependence, then all of the apparent rate coefficients ($k_f'$, $k_r'$, $k_f''$, and $k_r''$) and equilibrium constants ($K'$, $K''$, $K'''$, and $K''''$) will do so as well.

### *Deliverables*

If the mechanism is correct, the expression for the apparent rate of reaction (1) will take the form shown in equation (38). If additionally, O–✳ is the most abundant surface intermediate, it will take the form shown in equation (39). Experimental studies will need to be performed to determine whether either of these rate expressions captures the composition and temperature dependence of the rate with sufficient accuracy.

$$r_1 = \frac{k_f' \left[CO\right]^2 \left[O_2\right] - k_r' \left[CO_2\right]^2}{\left( \begin{array}{c} \left[CO_2\right] + K' \left[O_2\right] \left[CO_2\right] + K'' \left[CO\right] \left[O_2\right] \left[CO_2\right] \\ + K''' \left[CO\right] \left[O_2\right] + K'''' \left[CO\right]^2 \left[O_2\right] \end{array} \right)} \tag{38}$$

$$r_1 = k_f'' \left[CO\right] - k_r'' \frac{\left[CO_2\right]^2}{\left[CO\right]\left[O_2\right]} \tag{39}$$