

# A First Course on Kinetics and Reaction Engineering

## Activity 10.2

### Problem Purpose

This problem illustrates the generation of a rate expression from a mechanism for a heterogeneously catalyzed reaction and the simplification of that rate expression when there is a rate-determining step and a most abundant surface intermediate. *It also introduces the concept of a reactant-inhibited reaction.*

### Problem Statement

The oxidation of carbon monoxide is given in equation (1) below. Suppose that the mechanism is given by equations (2) through (4) and that step (4) is rate-limiting. Derive a rate expression in terms of only the partial pressures of the reagents and constants. How does the result change if O-\* is the most abundant surface intermediate? Comment upon the resulting rate expression.

Overall reaction:



Proposed mechanism:



### 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) and (3) 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. The assumption that O-\* is the most abundant surface intermediate can then be used to further simplify the resulting rate expression.

### 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 (5). This rate expression is of limited utility due to the appearance of surface coverages of O and CO. These quantities are difficult to measure, and it is preferred to eliminate them from the rate expression.

$$r_1 = r_{4,f} = k_{4,f} \theta_o \theta_{CO} \quad (5)$$

Because step (4) is rate-determining, reactions (2) and (3) may be assumed to be quasi-equilibrated. Corresponding equilibrium expressions are given in equations (6) and (7). This gives two equations with three surface coverages. The additional equation that we need is the conservation of active sites, equation (8).

$$K_2 = \frac{\theta_o^2}{P_{O_2} \theta_v} \quad (6)$$

$$K_3 = \frac{\theta_{CO}}{P_{CO} \theta_v} \quad (7)$$

$$\theta_v + \theta_o + \theta_{CO} = 1 \quad (8)$$

Equations (6) through (8) can be solved to obtain expressions for the fractional coverages of the three surface species. This can be performed manually or using symbolic algebra software. In either case, the results are given in equations (9) through (11).

$$\theta_v = \frac{1}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad (9)$$

$$\theta_o = \frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad (10)$$

$$\theta_{CO} = \frac{K_3 P_{CO}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad (11)$$

Substitution of equations (10) and (11) into equation (5) gives the desired rate expression in terms of only fluid-phase partial pressures and constants, equation (12).

$$r_1 = k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{\left(1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}\right)^2} \quad (12)$$

If O-\* is the most abundant surface intermediate, then its coverage will be much, much greater than that of the vacant sites, equation (13). Substituting equations (9) and (10) into equation (13) gives equation (14), which can be simplified leading to equation (15).

$$\theta_o \gg \theta_v \quad (13)$$

$$\frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \gg \frac{1}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad (14)$$

$$\sqrt{K_2 P_{O_2}} \gg 1 \quad (15)$$

Similarly, if O-\* is the most abundant surface intermediate, then its coverage will be much, much greater than the coverage of CO, equation (16). Substitution of equations (10) and (11) gives equation (17) which can be simplified to equation (18).

$$\theta_O \gg \theta_{CO} \quad (16)$$

$$\frac{\sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \gg \frac{K_3 P_{CO}}{1 + \sqrt{K_2 P_{O_2}} + K_3 P_{CO}} \quad (17)$$

$$\sqrt{K_2 P_{O_2}} \gg K_3 P_{CO} \quad (18)$$

Equations (15) and (18) indicate that the middle term in the denominator of the rate expression predominates, so the other terms can be dropped, leading to the rate expression given in equation (19).

$$r_1 \approx k_{4,f} \frac{K_3 P_{CO} \sqrt{K_2 P_{O_2}}}{(\sqrt{K_2 P_{O_2}})^2} = \frac{k_{4,f} K_3}{\sqrt{K_2}} \frac{P_{CO}}{\sqrt{P_{O_2}}} \quad (19)$$

The final rate expression is somewhat unusual in that it predicts that increasing the partial pressure of the reactant, O<sub>2</sub>, causes the rate of the reaction to decrease. This kind of behavior is referred to as reactant inhibition. Normally one expects that increasing the concentration or partial pressure of a reactant will cause the rate to increase, but here, reaction (1) is reactant-inhibited.