

# A First Course on Kinetics and Reaction Engineering

## Example 10.1

### Problem Purpose

This problem illustrates the generation of a rate expression from a mechanism for a heterogeneous catalytic reaction. In doing so, it also illustrates the use of the equation for the conservation of catalytic sites, and it shows how the assumption of a most abundant surface intermediate can simplify a mechanistic rate expression.

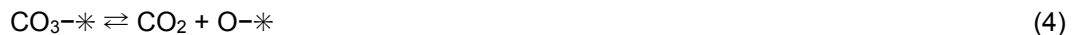
### Problem Statement

The oxidation of carbon monoxide is given in equation (1) below. Suppose that the mechanism is given by equations (2) through (6) and that step (6) 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?

Overall reaction:



Proposed mechanism:



### Problem Analysis

This problem asks us to generate a rate expression from a mechanism. It states that there is a rate-determining step, so the overall rate will be set equal to the rate of that step, and all other steps will be assumed to be quasi-equilibrated. The quasi-equilibrium expressions will be combined with the equation for the conservation of catalytic sites and solved to obtain expressions for the surface coverages. These will then be substituted into the rate expression. That rate expression then will be further simplified using the assumption that  $O^*$  is the most abundant surface intermediate.

### Problem Solution

Since step (6) is rate-determining, the overall rate is equal to the forward rate of step (6). Being elementary surface reactions, the rate expressions for each of the mechanistic steps are given by

equation (7). Thus, setting the rate of the non-elementary reaction (1) equal to the forward rate of step (6) leads to equation (8).

$$r_j = k_{j,f} \left( \prod_{\substack{i=\text{all} \\ \text{fluid phase} \\ \text{reactants}}} [i]^{-v_{i,j}} \prod_{\substack{m=\text{all} \\ \text{surface} \\ \text{reactants}}} \theta_m^{-v_{m,j}} \right) - k_{j,r} \left( \prod_{\substack{n=\text{all} \\ \text{fluid phase} \\ \text{products}}} [n]^{v_{n,j}} \prod_{\substack{l=\text{all} \\ \text{surface} \\ \text{products}}} \theta_l^{v_{l,j}} \right) \quad (7)$$

$$r_1 = r_6 = k_{6,f} \theta_{CO_2} \quad (8)$$

This is not acceptable because it contains the surface concentration of a reactive intermediates, namely  $CO_2^*$ . To eliminate the surface concentrations of the reactive intermediates, it can be noted that since step (6) is rate determining, then all other steps may be assumed to be quasi-equilibrated. Thus, equations (9) through (12) can be written expressing that steps (2) through (5) are quasi-equilibrated. Additionally, there is conservation of total catalyst sites, leading to equation (13). In these equations,  $\theta_v$  denotes the fraction of the surface sites that are vacant and the  $\theta_i$ 's represent the fractional coverage of the active sites by the various species,  $i$ .

$$K_2 = \frac{\theta_{O_2}}{P_{O_2} \theta_v} \quad (9)$$

$$K_3 = \frac{\theta_{CO_3}}{P_{CO} \theta_{O_2}} \quad (10)$$

$$K_4 = \frac{P_{CO_2} \theta_O}{\theta_{CO_3}} \quad (11)$$

$$K_5 = \frac{\theta_{CO_2}}{P_{CO} \theta_O} \quad (12)$$

$$1 = \theta_{O_2} + \theta_{CO_3} + \theta_O + \theta_{CO_2} + \theta_v \quad (13)$$

Equations (9) through (13) can be solved yielding expressions for the surface concentrations of the reactive intermediates in terms of only constants and partial pressures of stable species. The results are given in equations (14) through (18).

$$\theta_v = \frac{1}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}} \quad (14)$$

$$\theta_{O_2} = \frac{K_2 P_{O_2}}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}} \quad (15)$$

$$\theta_{CO_3} = \frac{K_2 K_3 P_{CO} P_{O_2}}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}} \quad (16)$$

$$\theta_O = \frac{\frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}}}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}} \quad (17)$$

$$\theta_{CO_2} = \frac{\frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}} \quad (18)$$

Finally equation (18) can be substituted into equation (8) leading to the desired rate expression in terms of only constants and partial pressures of stable species, equation (19).

$$r_1 = \frac{\frac{k_{6,f} K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}}{1 + K_2 P_{O_2} + K_2 K_3 P_{CO} P_{O_2} + \frac{K_2 K_3 K_4 P_{CO} P_{O_2}}{P_{CO_2}} + \frac{K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2}}}$$

$$r_1 = \frac{k_{6,f} K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}}{P_{CO_2} + K_2 P_{O_2} P_{CO_2} + K_2 K_3 P_{CO} P_{O_2} P_{CO_2} + K_2 K_3 K_4 P_{CO} P_{O_2} + K_2 K_3 K_4 K_5 P_{CO}^2 P_{O_2}} \quad (19)$$

If O\* is the most abundant surface intermediate, then equations (20) through (23) apply.

$$\theta_O \gg \theta_v \quad (20)$$

$$\theta_O \gg \theta_{CO_2} \quad (21)$$

$$\theta_O \gg \theta_{CO_3} \quad (22)$$

$$\theta_O \gg \theta_{O_2} \quad (23)$$

Substituting equations (14) and (17) into equation (20) leads to equation (24). Substituting equations (17) and (18) into equation (21) leads to equation (25). Substituting equations (16) and (17) into

equation (22) leads to equation (26). Substituting equations (15) and (17) into equation (23) leads to equation (27).

$$K_{1a}K_{1b}K_{1c}P_{CO}P_{O_2} \gg P_{CO_2} \quad (24)$$

$$K_{1a}K_{1b}K_{1c}P_{CO}P_{O_2} \gg K_{1a}K_{1b}K_{1c}K_{1d}P_{CO}^2P_{O_2} \quad (25)$$

$$K_{1a}K_{1b}K_{1c}P_{CO}P_{O_2} \gg K_{1a}K_{1b}P_{CO_2}P_{CO}P_{O_2} \quad (26)$$

$$K_{1a}K_{1b}K_{1c}P_{CO}P_{O_2} \gg K_{1a}P_{O_2}P_{CO_2} \quad (27)$$

Equations (24) through (27) show that the fourth term in the denominator of equation (19) is much larger than each of the other terms in the denominator. As a consequence, those terms can be dropped leaving only the fourth term as the entire denominator. Upon doing so, some quantities appear in both the numerator and the denominator, and they can be canceled. As a result, the original rate expression given in equation (19) reduces to equation (28) if O-\* is the most abundant surface intermediate.

$$r_1 = \frac{k_{6,f}K_2K_3K_4K_5P_{CO}^2P_{O_2}}{P_{CO_2} + K_2P_{O_2}P_{CO_2} + K_2K_3P_{CO}P_{O_2}P_{CO_2} + K_2K_3K_4P_{CO}P_{O_2} + K_2K_3K_4K_5P_{CO}^2P_{O_2}}$$

$$\approx \frac{k_{6,f}K_2K_3K_4K_5P_{CO}^2P_{O_2}}{K_2K_3K_4P_{CO}P_{O_2}}$$

$$r_1 = k_{6,f}K_5P_{CO} \quad (28)$$