

## Activity 10.1

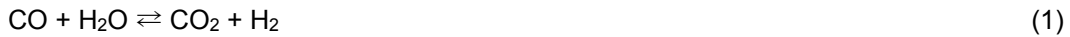
### Problem Purpose

This problem illustrates the generation of a rate expression from a mechanism for a heterogeneously catalyzed reaction.

### Problem Statement

The water-gas shift reaction, equation (1), might take place according to the mechanism given in equations (2) and (3). Find an expression for the rate of water-gas shift in terms of the partial pressures of fluid phase species and constants.

Overall, macroscopically observed reaction:



Postulated mechanism:



### Problem Analysis

This problem asks us to generate a rate expression from a mechanism for a heterogeneous catalytic reaction. No step is identified as rate-determining, so the rate of the macroscopically observed reaction with respect to a reagent in that reaction will be set equal to the sum of the rates of generation of that reagent in the mechanistic steps. The concentrations of reactive intermediates in that expression will then be eliminated using the Bodenstein steady state approximation and the conservation of sites.

### Problem Solution

The rate of the apparent, macroscopically observed reaction (1) is found using equation (4), where the index  $s$  will range from 2 to 3. The rates of mechanistic steps taking place on a solid surface are given by equation (5). Combining these equations and applying them to the product  $\text{H}_2$  (i. e.  $i = \text{H}_2$ ) gives equation (6).

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{i,s} r_s \quad (4)$$

$$r_j = k_{j,f} \left( \prod_{\substack{i=\text{all} \\ \text{fluid phase} \\ \text{reactants}}} [i]^{-\nu_{i,j}} \prod_{\substack{m=\text{all} \\ \text{surface} \\ \text{reactants}}} \theta_m^{-\nu_{m,j}} \right) - k_{j,r} \left( \prod_{\substack{n=\text{all} \\ \text{fluid phase} \\ \text{products}}} [n]^{\nu_{n,j}} \prod_{\substack{l=\text{all} \\ \text{surface} \\ \text{products}}} \theta_l^{\nu_{l,j}} \right) \quad (5)$$

$$r_{\text{H}_2,1} = k_{3,f} P_{\text{H}_2\text{O}} \theta_v - k_{3,r} P_{\text{H}_2} \theta_{\text{O}} \quad (6)$$

This rate expression is not acceptable because it contains the concentration of reactive intermediates, namely the fractional surface coverage of O and vacant surface sites. To eliminate the surface concentrations of reactive intermediates from the rate expression, the Bodenstein steady-state approximation can be applied to each reactive intermediate as given in equation (7). However, if the Bodenstein steady-state approximation is applied to both reactive intermediates, the resulting equations will not be mathematically independent. Therefore, equation (7) is only applied to one of the reactive intermediates; here the vacant site was used, resulting in equation (8). In place of the other Bodenstein steady state approximation, a statement of the conservation of total catalyst is used, as given in equation (9).

$$0 = \sum_{\substack{s=\text{all} \\ \text{steps}}} v_{i,s} r_s \quad (i = \text{reactive intermediate}) \quad (7)$$

$$0 = (k_{2,f} P_{CO} \theta_O - k_{2,r} P_{CO_2} \theta_v) - (k_{3,f} P_{H_2O} \theta_v - k_{3,r} P_{H_2} \theta_O) \quad (8)$$

$$1 = \theta_O + \theta_v \quad (9)$$

Equations (8) and (9) can be solved to obtain expressions for the concentrations of each of the reactive intermediates in terms of only constants and the partial pressures of stable species. This can be done manually or using symbolic algebra software, in either case, the results are given in equations (10) and (11).

$$\theta_v = \frac{k_{2,f} P_{CO} + k_{3,r} P_{H_2}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}} \quad (10)$$

$$\theta_O = \frac{k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}} \quad (11)$$

Finally, equations (10) and (11) can be substituted into equation (6) to obtain the desired rate expression, equation (12).

$$r_{H_2,1} = \frac{k_{2,f} k_{3,f} P_{CO} P_{H_2O} - k_{2,r} k_{3,r} P_{CO_2} P_{H_2}}{k_{2,f} P_{CO} + k_{2,r} P_{CO_2} + k_{3,f} P_{H_2O} + k_{3,r} P_{H_2}} \quad (12)$$