A First Course on Kinetics and Reaction Engineering

Example 4.1

Problem Purpose

This example illustrates the conversion between a generalized rate and the rate with respect to a species, the normalization of a rate expression and other aspects of rates and rate expressions.

Problem Statement

Reaction (1) is catalyzed by the surface of a solid catalyst. A 1 g sample of the catalyst has a surface area of 87 m^2. A student took a 2.7 L vessel that had 1.6 g of the catalyst in it and filled it with a mixture of 25% CO, 25% CO_2 and 50% H_2 at 0.5 MPa and 550 K and then measured the initial rate at which methanol was formed. The measured value was 1.07 x 10^{-3} moles of CH_3OH formed per minute.

(a) At the conditions the student studied, what is the best value for the rate of reaction (1) with respect to H_2?

(b) At the conditions the student studied, what is the best value for the generalized rate of reaction (1)?

(c) What is the mathematical form of the rate expression for reaction (1)?

(d) The student was asked to repeat the experiment a week later, but the only vessel available had a volume of 10 L. The student put 1.6 g of the catalyst in the 10 L vessel and then filled it with a mixture of 25% CO, 25% CO_2 and 50% H_2 at 0.5 MPa and 550 K. If the original rate measurement was accurate, at what rate (moles per minute) will methanol initially form in this experiment?

$$CO + 2\,H_2 \rightleftarrows CH_3OH \tag{1}$$

Problem Solution

(a) The best value for any of the rates will be the rate that is normalized by the catalyst surface area since the reaction takes place only on that surface and not everywhere within the volume. The rate with respect to methanol can be calculated using the information given.

$$r_{CH_3OH,1} = \frac{1}{A_{cat}}\frac{dn_{CH_3OH}}{dt}$$

$$r_{CH_3OH,1} = \frac{1}{(1.6\text{ g})\left(87\text{m}^2 g^{-1}\right)}\left(1.07\times 10^{-3}\text{mol min}^{-1}\right)$$

$$r_{CH_3OH,1} = 7.69 \text{ x } 10^{-6} \text{ mol min}^{-1} \text{ m}^{-2}$$

The problem asks for the rate with respect to H_2, and that can be found using the definition of the generalized rate of reaction.

$$r_1 = \frac{r_{CH_3OH,1}}{\nu_{CH_3OH,1}} = \frac{r_{H_2,1}}{\nu_{H_2,1}}$$

$$r_{H_2,1} = \frac{\nu_{H_2,1}}{\nu_{CH_3OH,1}} r_{CH_3OH,1} = \frac{-2}{1} r_{CH_3OH,1} = -1.54 \text{ x } 10^{-5} \text{ mol min}^{-1} \text{ m}^{-2}$$

(b) The generalized rate is found from the rate with respect to methanol by definition.

$$r_1 = \frac{r_{CH_3OH,1}}{\nu_{CH_3OH,1}} = \frac{r_{CH_3OH,1}}{1} = 7.69 \text{ x } 10^{-6} \text{ mol min}^{-1} \text{ m}^{-2}$$

(c) There is no way of telling what the mathematical form of the rate expression will be without doing experiments.

(d) The temperature, pressure and composition are the same as in the first experiment, so the specific rate (moles per minute per m^2 of catalyst) will also be the same. The amount of catalyst was also the same as in the first experiment, and hence the total catalyst surface area was also the same. Therefore, the change in volume will not affect the number of moles of methanol produced per minute; it will still equal 1.07 x 10^{-3} moles per minute.