A First Course on Kinetics and Reaction Engineering

Example 4.2

Problem Purpose

This example illustrates the conversion from one normalization factor to another one and the conversion of a rate or rate expression with respect to one reagent to a rate or rate expression with respect to a different reagent.

Problem Statement

Rase [1] gives equation (1) as the expression for the rate of ammonia synthesis, equation (2), with respect to ammonia. In equation (1), a_i denotes the thermodynamic activity of species i, E_2 is the (known) activation energy, R is the gas constant and $K(T)$ is the (dimensionless) equilibrium constant. Write an expression for the rate with respect to hydrogen where the rate is normalized using the surface area of the catalyst.

$$r_{NH_3,2} = 1.54 \times 10^{15} \exp\left(\frac{-E_2}{RT}\right)\left[K(T)^2\left(\frac{a_{N_2}a_{H_2}^{3/2}}{a_{NH_3}}\right) - \frac{a_{NH_3}}{a_{H_2}^{3/2}}\right]\frac{\text{kmol NH}_3}{\text{m}_{\text{cat}}^3\text{ h}} \tag{1}$$

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 \tag{2}$$

The ammonia synthesis catalyst takes the form of pellets that pack into the reactor with a bulk density of 165 lb ft^{-3}. Assume the surface area of this catalyst to equal 78 $m^2\ g^{-1}$.

1. Rase, H.F., *Chemical Reactor Design for Process Plants*. Vol. Two. 1977, New York: John Wiley. 242.

Problem Solution

The problem states that equation (1) is the rate of reaction (2) with respect to ammonia, $r_{NH_3,2}$. Examining the units reveals that the rate was normalized using the volume of the catalyst. Here we will take this to equal the bed volume (catalyst plus void space), since we are given the bulk density of the catalyst (which is the mass per bed volume). The rate of reaction with respect to species i is related to the rate of the same reaction with respect to species k according to equation (3).

$$\frac{r_{i,j}}{\nu_{i,j}} = \frac{r_{k,j}}{\nu_{k,j}} \tag{3}$$

The rate with respect to hydrogen is found by substitution of the information provided in the problem statement along with the stoichiometric coefficients from reaction (2).

$$\frac{r_{NH_3,2}}{\nu_{NH_3,5.2B}2} = \frac{r_{H_2,2}}{\nu_{H_2,2}}$$

$$r_{H_2,2} = \frac{\nu_{H_2,2}}{\nu_{NH_3,2}} r_{NH_3,2}$$

$$r_{H_2,2} = \frac{-3}{2}\left(1.54\times10^{15}\exp\left(\frac{-E_2}{RT}\right)\left[K(T)^2\left(\frac{a_{N_2}a_{H_2}^{3/2}}{a_{NH_3}}\right)-\frac{a_{NH_3}}{a_{H_2}^{3/2}}\right]\frac{\text{kmol NH}_3}{\text{m}_{\text{cat}}^3\ \text{h}}\right)$$

$$r_{H_2,2} = -2.31\times10^{15}\exp\left(\frac{-E_2}{RT}\right)\left[K(T)^2\left(\frac{a_{N_2}a_{H_2}^{3/2}}{a_{NH_3}}\right)-\frac{a_{NH_3}}{a_{H_2}^{3/2}}\right]\frac{\text{kmol NH}_3}{\text{m}_{\text{cat}}^3\ \text{h}}$$

To renormalize the rate expression, one simply multiplies by the old normalization factor and divides by the new one.

$$\begin{aligned}r_{H_2,2} &= -2.31\times10^{15}\exp\left(\frac{-E_2}{RT}\right)\left[K(T)^2\left(\frac{a_{N_2}a_{H_2}^{3/2}}{a_{NH_3}}\right)-\frac{a_{NH_3}}{a_{H_2}^{3/2}}\right]\frac{\text{kmol NH}_3}{\text{m}_{\text{cat}}^3\ \text{h}}\\ &\quad\times\left(\frac{\text{ft}^3}{165\text{ lb}}\right)\times\left(0.0283\frac{\text{m}^3}{\text{ft}^3}\right)\times\left(\frac{\text{lb}}{454\text{ g}}\right)\times\left(\frac{\text{g}}{78\text{ m}^2}\right)\\ &= -1.12\times10^{7}\exp\left(\frac{-E_2}{RT}\right)\left[K(T)^2\left(\frac{a_{N_2}a_{H_2}^{3/2}}{a_{NH_3}}\right)-\frac{a_{NH_3}}{a_{H_2}^{3/2}}\right]\frac{\text{kmol NH}_3}{\text{m}_{\text{cat}}^2\ \text{h}}\end{aligned}$$