Web 15.3.3 Effectiveness Factor for Nonisothermal First-Order Catalytic Reactions

The preceding discussion of effectiveness factors is valid only for isothermal conditions. When a reaction is exothermic and nonisothermal, the effectiveness factor can be significantly greater than 1, as shown in Figure W15-7. Values of \( \eta \) greater than 1 occur because the external surface temperature of the pellet is less than the temperature inside the pellet where the exothermic reaction is taking place. Therefore, the rate of reaction inside the pellet is greater than the rate at the surface. Thus, because the effectiveness factor is the ratio of the actual reaction rate to the rate at surface conditions, the effectiveness factor can be greater than 1, depending on the magnitude of the parameters \( \beta \) and \( \gamma \).

The parameter \( \gamma \) is sometimes referred to as the Arrhenius number, and the parameter \( \beta \) represents the maximum temperature difference that could exist in the pellet relative to the surface temperature \( T_s \).

\[
\gamma = \text{Arrhenius number} = \frac{E}{RT_s} \\
\beta = \frac{\Delta T_{\text{max}}}{T_s} = \frac{T_{\text{max}} - T_s}{T_s} = \frac{-\Delta H_R D_e C_{A_s}}{k_t T_s}
\]

Can you find regions where multiple solutions (MSS) exist?

**Figure W15-7** Nonisothermal effectiveness factor.
(See Web Problem P15-13C for the derivation of $\beta$.) The Thiele modulus for a first-order reaction, $\phi_1$, is evaluated at the external surface temperature. Typical values of $\gamma$ for industrial processes range from a value of $\gamma = 6.5$ ($\beta = 0.025$, $\phi_1 = 0.22$) for the synthesis of vinyl chloride from HCl and acetone, to a value of $\gamma = 29.4$ ($\beta = 6 \times 10^{-3}$, $\phi_1 = 1.2$) for the synthesis of ammonia. The lower the thermal conductivity $k_t$ and the higher the heat of reaction, the greater the temperature difference (see Problems P15-13C and P15-14C). We observe from Figure W15-7 that multiple steady states can exist for values of the Thiele modulus less than 1 and when $\beta$ is greater than approximately 0.2. There will be no multiple steady states when the criterion developed by Luss is fulfilled.  

$$4(1+\beta) > \beta \gamma$$  \hspace{1cm} (W15-36)

**Web Problem.** Suppose we let $\gamma = 30$, $\beta = 0.4$, and $\phi_1 = 0.4$ in Figure W15-7? What would cause you to go from the upper steady state to the lower steady state and vice versa?

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