

A First Course on Kinetics and Reaction Engineering

Unit 7. The Steady State Approximation

Definitions

steady state - value(s) not changing with time

kinetically insignificant (reaction) - a mechanistic step for which the rate does not affect the rate of the apparent, macroscopically observed reaction

Nomenclature

[] symbols indicating the concentration or, if a gas, partial pressure of the species within the brackets

$v_{i,j}$ stoichiometric coefficient of species i in reaction j

k_j rate coefficient for reaction j , an additional subscripted “ f ” indicates rate coefficient for the absolute rate in the forward direction and “ r ” denotes the reverse direction

$r_{i,j}$ rate of generation of species i via reaction j , or, equivalently, the rate of reaction j with respect to species i

r_j generalized net rate of reaction j

Equations

$$r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} v_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-v_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{v_{n,s}} \right) \quad (7.1)$$

$$r_s = 0 \quad s = \text{kinetically insignificant step} \quad (7.2)$$

$$r_s = k_{s,f} \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-v_{i,s}} \quad s = \text{irreversible step} \quad (7.3)$$

$$0 = \sum_{\substack{s=\text{all} \\ \text{steps}}} v_{i,s} \left(k_{s,f} \prod_{\substack{m=\text{all} \\ \text{reactants}}} [m]^{-v_{m,s}} - k_{s,r} \prod_{\substack{n=\text{all} \\ \text{products}}} [n]^{v_{n,s}} \right) \quad i = \text{reactive intermediate} \quad (7.4)$$