A First Course on Kinetics and Reaction Engineering
Unit 17. Reactor Models and Reaction Types

Definitions

Auto-thermal reactions - reactions for which the heat released by the reaction ($-\Delta H$) is sufficient to raise the temperature of the fresh reactants to a point where the reaction will proceed spontaneously without the addition of heat from any external source

Auto-catalytic reactions - reactions where the rate of reaction increases as the concentration of a product increases

Reactant-inhibited reactions - reactions where an increase in the concentration of a reactant leads to a decrease in the reaction rate

Product-inhibited reactions - reactions where an increase in the concentration of a product leads to a decrease in the reaction rate

Series reaction networks - a group of chemical reactions wherein the product of one reaction is a reactant in another reaction

Parallel reaction networks - a group of chemical reactions that share a common reactant

Series-parallel reaction networks - a group of chemical reactions wherein the product of one reaction is a reactant in another reaction and all of the reactions share a common co-reactant

Nomenclature

ΔG_j standard Gibbs free energy change for reaction j

ΔH_j heat of reaction j

ΔS_j entropy change for reaction j

Φ_s sphericity of the packing in a packed bed

ε bed porosity

μ fluid viscosity

μ_{max} parameter in the Monod equation for the rate of cell growth

$\nu_{i,j}$ stoichiometric coefficient of species i in reaction j; value is positive for products and negative for reactants

ρ fluid density

A cross-sectional area available to flow inside a PFR

C_i molar concentration of species i

$\hat{C}_{p,i}$ constant pressure specific molar heat capacity of species i

D inside diameter of a PFR; a subscripted p denotes a particle diameter

G mass velocity (mass flow divided by tube cross sectional area)

K_j equilibrium constant for reaction j; a subscripted 0 denotes the entropy term when the entropy and enthalpy are taken to be constants (i. e. the equivalent of a rate coefficient pre-exponential factor); a subscripted s indicates the saturation constant in the Monod equation for the rate of cell growth

P pressure

$\dot{Q}$ net heat input into a reactor through its walls or the walls of a submerged cooling coil

R ideal gas constant

T temperature; a subscripted e denotes the (external) temperature of the heat transfer media

U overall heat transfer coefficient for heat transfer through the wall of a tubular reactor

V reactor volume within which reaction takes place

$\dot{V}$ volumetric flow rate; a superscripted zero denotes the value at the reactor inlet

$\dot{W}$ net rate at which mechanical work is done by a reactor system on its surroundings through shafts and moving boundaries

f friction factor

g_c gravitational constant (a unit conversion factor, not the acceleration due to gravity)

k_j rate coefficient for reaction j; primes are used to distinguish between multiple rate coefficients for the same reaction

$k_{0,j}$ pre-exponential factor in the Arrhenius expression for the temperature dependence of the rate coefficient for reaction j

n_i moles of species i; a superscripted zero denotes the value at the start of the reaction

$\dot{n}_i$ molar flow rate of species i; a superscripted zero denotes the value at the reactor inlet

r_j the generalized rate of reaction j

t time

z axial distance from the inlet to a PFR

Equations

INPUT + GENERATION = OUTPUT + ACCUMULATION (17.1)

$$\frac{dn_i}{dt} = V \sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j \tag{17.2}$$

$$\dot{Q} - \dot{W} = \frac{dT}{dt} \sum_{\substack{i=all\\species}} \left(n_i \hat{C}_{pi} \right) + V \sum_{\substack{j=all\\reactions}} \left(r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt} \tag{17.3}$$

$$\frac{\dot{n}_i}{\dot{V}} \frac{dV}{dt} + \frac{V}{\dot{V}} \frac{d\dot{n}_i}{dt} - \frac{\dot{n}_i V}{\dot{V}^2} \frac{d\dot{V}}{dt} = \dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=all\\reactions}} \nu_{i,j} r_j \tag{17.4}$$

$$\begin{aligned}\dot{Q}-\dot{W} &= \sum_{\substack{i=all\\species}}\left(\dot{n}_i^0\int_{T^0}^{T}\hat{C}_{pi}\,dT\right)+V\sum_{\substack{j=all\\reactions}}\left(r_j\Delta H_j\big|_T\right)\\ &\quad+\frac{V}{\dot{V}}\sum_{\substack{i=all\\species}}\left(\dot{n}_i\hat{C}_{pi}\right)\left(\frac{dT}{dt}\right)-V\left(\frac{dP}{dt}\right)-P\left(\frac{dV}{dt}\right)\end{aligned} \tag{17.5}$$

$$\frac{\partial \dot{n}_i}{\partial z}=\frac{\pi D^2}{4}\sum_{\substack{j=all\\reactions}}\nu_{i,j}r_j-\frac{\pi D^2}{4\dot{V}}\frac{\partial \dot{n}_i}{\partial t}+\frac{\pi D^2\dot{n}_i}{4\dot{V}^2}\frac{\partial \dot{V}}{\partial t} \tag{17.6}$$

$$\begin{aligned}\pi DU\left(T_e-T\right) &= \left(\sum_{\substack{i=all\\species}}\dot{n}_i\hat{C}_{pi}\right)\frac{\partial T}{\partial z}+\frac{\pi D^2}{4}\sum_{\substack{j=all\\reactions}}\left(r_j\Delta H_j\right)\\ &\quad+\frac{\pi D^2}{4\dot{V}}\sum_{\substack{i=all\\species}}\left(\dot{n}_i\hat{C}_{pi}\right)\frac{\partial T}{\partial t}-\frac{\pi D^2}{4}\frac{\partial P}{\partial t}\end{aligned} \tag{17.7}$$

$$0=\dot{n}_i^0-\dot{n}_i+V\sum_{\substack{j=all\\reactions}}\nu_{i,j}r_j \tag{17.8}$$

$$\dot{Q}-\dot{W}=\sum_{\substack{i=all\\species}}\left(\dot{n}_i^0\int_{T^0}^{T}\hat{C}_{pi}\,dT\right)+V\sum_{\substack{j=all\\reactions}}\left(r_j\Delta H_j\big|_T\right) \tag{17.9}$$

$$\frac{\partial \dot{n}_i}{\partial z}=\frac{\pi D^2}{4}\sum_{\substack{j=all\\reactions}}\nu_{i,j}r_j \tag{17.10}$$

$$\pi DU\left(T_e-T\right)=\left(\sum_{\substack{i=all\\species}}\dot{n}_i\hat{C}_{pi}\right)\frac{\partial T}{\partial z}+\frac{\pi D^2}{4}\sum_{\substack{j=all\\reactions}}\left(r_j\Delta H_j\right) \tag{17.11}$$

$$\frac{\partial P}{\partial z}=-\frac{G}{g_c}\left(\frac{4}{\pi D^2}\right)\frac{\partial \dot{V}}{\partial z}-\frac{2fG^2}{\rho D} \tag{17.12}$$

$$\frac{\partial P}{\partial z}=-\frac{1-\varepsilon}{\varepsilon^3}\frac{G^2}{\rho\Phi_s D_p g_c}\left[\frac{150\left(1-\varepsilon\right)\mu}{\Phi_s D_p G}+1.75\right] \tag{17.13}$$

$$K_j=\exp\left\{\frac{-\Delta G_j}{RT}\right\}=\exp\left\{\frac{\Delta S_j}{R}\right\}\exp\left\{\frac{-\Delta H_j}{RT}\right\} \tag{17.14}$$

$$K_j = K_{0,j} \exp\left\{\frac{-\Delta H_j}{RT}\right\} \tag{17.15}$$

A + B → Y + Z (17.16)

$$r_{17.16} = k_{0,17.16} \exp\left\{\frac{-E_{17.16}}{RT}\right\} C_A C_B \tag{17.17}$$

A + B ⇄ Y + Z (17.18)

$$r_{17.18} = k_{17.18} \exp\left\{\frac{-E_{17.18}}{RT}\right\} C_A C_B \left[1 - \frac{C_Y C_Z}{K_{0,17.18} \exp\left\{\frac{-\Delta H_{17.18}}{RT}\right\} C_A C_B}\right] \tag{17.19}$$

2 S → X (17.20)

$$r_{17.20} = \frac{\mu_{max} C_X C_S}{K_s + C_S} \tag{17.21}$$

$$r_{17.16} = \frac{k_{17.16} C_A C_B}{1 + k'_{17.16} C_Y} \tag{17.22}$$

$$r_{17.16} = \frac{k_{17.16} C_A C_B}{1 + k'_{17.16} C_B^2} \tag{17.23}$$

A → D (17.24)

D → U (17.25)

A → B → C → D → …. (17.26)

A → D (17.27)

A → U (17.28)

A + B → Y (17.29)

Y + B → Z (17.30)