Unsteady Operation

Unsteady mole balance for liquid phase reactions in a CSTR

$$\tau\frac{dC_A}{dt} = C_{A0} - C_A + \underbrace{r_A\tau}_{-(-r_A)\tau} \qquad (1)$$

At steady state

$$0 = C_{A0} - C_{AS} - (-r_S)\tau \qquad (2)$$

adding Equation (1) and (2)

$$\boxed{\tau\frac{dC_A}{dt} = -(C_A - C_{AS}) - \left[(-r_A) - (-r_{AS})\right]\tau} \qquad (3)$$

The unsteady energy balance is

$$\frac{dT}{dt} = \frac{F_{A0}\left[G(T) - R(T)\right]}{\sum N_i C_{P_i}} \qquad (4)$$

We are going to make the following approximation

$$\sum N_i C_{P_i} = N_A C_{P_A} + N_B C_{P_B} = N_{A0} C_{P_S} = VC_{A0}C_{P_S} \qquad (5)$$

Eubstituting Equation (5) into Equation (4) and considering the G(T) (Term 1) and R(T) (Term 2) separately

Term 1: $$\frac{F_{A0}G(T)}{VC_{A0}C_{P_S}} = \frac{F_{A0}\left(-r_A V/F_{A0}\right)\left(-\Delta H_{Rx}\right)}{VC_{A0}C_{P_S}} = -r_A\underbrace{\left[\frac{-\Delta H_{Rx}}{C_{A0}C_{P_S}}\right]}_{J} \qquad (6)$$

$$= -r_A J \qquad (7)$$

Term 2: $$\frac{F_{A0}R(T)}{VC_{A0}C_{P_S}} = \frac{v_0 C_{A0}\left[C_{P_S}(1+\kappa)(T - T_C)\right]}{VC_{A0}C_{P_S}} = \frac{(1+\kappa)(T - T_C)}{\tau} \qquad (8)$$

Substituting Equations (7) and (8) into Equation (4) we obtain

$$\tau\frac{dT}{dt} = -r_A J\tau - (1+\kappa)(T - T_C) \qquad (9)$$

At steady state

$$0 = -r_A J\tau - (1+\kappa)(T_S - T_C) \qquad (10)$$

Adding Equations (9) and (10)

$$\boxed{\tau\frac{dT}{dt} = J\tau\left[(-r_A) - (-r_S)\right] - (1+\kappa)(T - T_S)}$$

Expanding $-r_A$ in a Taylor series about the steady state

$$-r_A = -r_{AS} + \left(C_A - C_{AS}\right)\left.\frac{\partial\left(-r_A\right)}{\partial C_A}\right|_S + \left(T - T_S\right)\left.\frac{\partial\left(-r_A\right)}{\partial T}\right|_S$$

$$\left[\left(-r_A\right) - \left(-r_S\right)\right] = k_S\left(C_A - C_{AS}\right) + \left(T - T_S\right)\frac{E}{RT_S^2}\left(-r_{AS}\right)$$

$$\tau\frac{dC_A}{dt} = -\left(C_A - C_{AS}\right) - \tau k\left(C_A - C_{AS}\right) - \tau\frac{E}{RT_S}\left(-r_{AS}\right)\left(T - T_S\right)$$

$$\theta = t/\tau$$

$$x = C_A - C_{AS}$$

$$y = T - T_S$$

$$\frac{dx}{d\theta} = -\underbrace{\left(1 + \tau k_S\right)}_{A}X - \underbrace{\frac{JE\tau\left(-r_{AS}\right)}{RT_S^2}}_{B}\frac{y}{J}$$

$$A = 1 + \tau k_S$$

$$B = \frac{\tau JE\left(-r_{AS}\right)}{RT_S^2}$$

$$C = \left(1 + \kappa\right)$$

$$\boxed{\frac{dx}{d\theta} = -Ax - B\frac{y}{J}}$$

$$\tau\frac{dT}{dt} = -J\left[\tau k_S\left(C_A - C_{AS}\right) + \frac{E\left(-r_{AS}\right)}{RT_S^2}\left(T - T_S\right)\right] - \left(1 + \kappa\right)\left(T - T_S\right)$$

$$\frac{dy}{d\theta} = J\tau k_S x + By - Cy$$

$$\frac{dy}{d\theta} = J\left(A - 1\right)x + \left(B - C\right)y$$

$$\boxed{\frac{dx}{d\theta} = -Ax - \frac{By}{J}}$$

$$\boxed{\frac{dy}{d\theta} = -J\left(A - 1\right)x + \left(B - C\right)y}$$

$$x = K_1 e^{\lambda_1 t} + K_2 e^{\lambda_2 t}$$

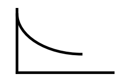
$$y = K_3 e^{\lambda_1 t} + K_4 e^{\lambda_2 t}$$

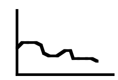
$$\lambda_1, \lambda_2 = \frac{Tr \pm \sqrt{T_R^2 - 4Det}}{2}$$

$$\boxed{Tr = -A + B - C = B - (A + C)}$$

$$Det = AC - B$$

$Tr < 0$ $Det > 0$ Stable

$\left(T_r^2 - 4Det\right) > 0$ 

$\left(T_r^2 - 4Det\right) < 0$ 

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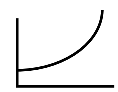
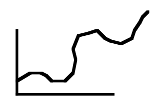
$\left[T_r^2 - 4Det\right] > 0$ 

$\left[T_r^2 - 4Det\right] < 0$ 

$Tr = 0$ $Det > 0$ Pure Oscillation