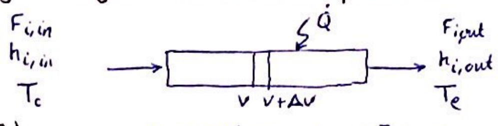
(1) Ideal Non-Isothermal PFRs

- Consider the general EBE
  - $\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_i F_{i,in} h_{i,in} - \sum_i F_{i,out} h_{i,out}$
  - In most instances $\dot{W}_s$ term can be neglected.
  - Also for SS op: $dE_{sys}/dt = 0$
  - hence, the EBE for the entire reactor is given by: $\dot{Q} + \sum_i F_{io} h_{io} - \sum_i F_{ie} h_{ie} = 0$ (I)
  - however, F_i and h_i vary since comp. and T vary along the length of PFR as the rxn proceeds.

h_{io} and h_{ie} are specific enthalpy $[\frac{J}{mol}]$ at inlet and exit conditions resp.

- general EBE on a ΔV element
  - would be: $\Delta\dot{Q} + \left(\sum_i F_i h_i\right)_V - \left(\sum_i F_i h_i\right)_{V+\Delta V} = 0$ (II)
  - eq. II in terms of specific enthalpy on a mass basis

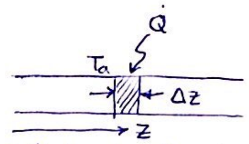


$F_i \triangleq [mol/s]$, $h_i \equiv [J/mol]$

(II) $\Rightarrow$ $\Delta\dot{Q} + \left(\sum_i \dot{m}_i h_i'\right)_V - \left(\sum_i \dot{m}_i h_i'\right)_{V+\Delta V} = 0$ (III) $\quad (h_i' \equiv [J/kg])$

  - let h' be the specific enthalpy of the reacting mixture (mass basis). and it is defined as: $h' = \frac{\sum_i \dot{m}_i h_i'}{\sum_i \dot{m}_i}$ (IV)
  - (IV) into (III) $\Rightarrow$ $\Delta\dot{Q} + \left[\left(\sum_i \dot{m}_i\right) h'\right]_V - \left[\left(\sum_i \dot{m}_i\right) h'\right]_{V+\Delta V} = 0$ (V)
  - but
    - $\sum_i \dot{m}_i = \dot{m} \triangleq$ total mass flow rate
    - and $\dot{m}$ remains the same due to conservation of mass.
  - hence, (V) $\Rightarrow$ $\Delta\dot{Q} + \dot{m}\left(h'|_V - h'|_{V+\Delta V}\right) = 0$ (VI)

- The $\Delta\dot{Q}$ Term
  - let z be distance along the length of PFR
  - $\Delta\dot{Q} = U_o(\Delta A)(T_a - T)$
  - $\Delta A = \pi D \Delta z$, $\Delta V = \frac{\pi D^2}{4}\Delta z \Rightarrow \Delta z = \frac{4\Delta V}{\pi D^2}$
  - $\Rightarrow \Delta\dot{Q} = \frac{4U_o}{D}\Delta V (T_a - T)$



$D \triangleq$ diameter of reactor

- back to (VI)
  - $\Rightarrow \dot{m}\left(h|_{V+\Delta V} - h|_V\right) = \frac{4U_o}{D}\Delta V(T_a - T)$ (VI)
  - taking the limit as $\Delta V \to 0$ $\Rightarrow$ $\boxed{\dot{m}\frac{dh'}{dt} = \frac{4U_o}{D}(T_a - T)}$ (VII)

- Specific Enthalpy
  - Due to sensible heat: $\dot{m}\frac{dh'_{thermal}}{dV} = \dot{m}c_p'\frac{dT}{dV}$
    - units: $\frac{kg}{s}$, $\frac{J/kg}{m^3}$, $\frac{kg}{s}$, $\frac{J}{kg\cdot k}$, $\frac{k}{m^3}$

c_p' is on a mass basis

  - Due to energy released or consumed in chemical rxn: $\dot{m}\frac{dh'_{chemical}}{dV} = (\Delta H_{R,A})(-r_A)$
    - units: $\frac{J}{mol}$, $\frac{mol}{m^3 \cdot s}$
  - hence, eq. VII becomes: $\dot{m}c_p'\frac{dT}{dV} + (\Delta H_{R,A})(-r_A) = \frac{4U_o}{D}(T_a - T)$
    $\Rightarrow \boxed{\frac{dT}{dV} = \frac{4U_o}{\dot{m}c_p' D}(T_a - T) - \frac{(\Delta H_{R,A})(-r_A)}{\dot{m}c_p'}}$ (VIII)
  - or if the heat capacities are expressed in a molar basis: $\boxed{\frac{dT}{dV} = \frac{\frac{4U_o}{D}(T_a - T) - (\Delta H_{R,A})(-r_A)}{\sum_i F_i C_{pi}}}$ (IX)

- The comp. balance eq. for a PFR is given by: $\boxed{\frac{dX_A}{dV} = \frac{1}{F_{Ao}}(-r_A)}$ (X)
- To obtain T and X_A as a function of PFR volume, we must solve the above system of ODEs simultaneously.
- Note that
  - $(-r_A)$ must be expressed in terms of X_A and T
  - C_{pi}, $\Delta H_{R,A}$ " " " as a function of T.
  - F_i as functions of X_A

- Ex. 01 → "Non-Isothermal PFR"
  - → gas phase rxn, ideal gases, $\underset{A}{CH_4} + \underset{B}{Cl_2} \longrightarrow \underset{C}{CH_2Cl_2} + \underset{D}{HCl}$, $-r_A = -r_B = kC_AC_B = 7.5\times10^{11}\times e^{\frac{-17940}{T}} C_AC_B$ $[\frac{mol}{m^3.s}]$
  - → PFR: $D = 7.5^{cm}$, $V_R = 2^{m^3}$, $F_{A_0} = 24^{mol/s}$, $F_{B_0} = 6^{mol/s}$, $P_0 = 0.2^{MPa}$ (constant)
  - → $T_a = T_0$ (inlet Feed T) , $\Delta H^o_{R,298} = -23^{kcal/mol}$, $C_{P,A} = 17.10^{cal/mol.k}$, $C_{P,B} = 8.75^{cal/mol.k}$
  - → T and X_B profiles for → $T_0 = 530^k$, U_0 between $0-30$ $^{cal/m^2.s.k}$; → $U_0 = 30$ $^{cal/m^2.s.k}$, T_0 between $530-540^k$; $C_{P,C} = 10.01^{cal/mol.k}$, $C_{P,D} = 7.07^{cal/mol.k}$

- Ex. 01 Solution "MBE"
  - → Comp. B is the limiting reactant $\Rightarrow -r_B = -\frac{dF_B}{dV} = F_{B_0}\frac{dX_B}{dV} = kC_AC_B$
  - → stoichiometric table:

$$C_A = \frac{F_A}{F_t}C_t = \frac{F_{A_0} - F_{B_0}X_B}{F_{A_0} + F_{B_0}} \times \frac{P_0}{RT}$$

$$C_B = \frac{F_{B_0}(1-X_B)}{F_{A_0}+F_{B_0}} \times \frac{P_0}{RT}$$

Comp.	@ inlet	@ any point	in terms of X_B
A	F_{A_0}	F_A	$F_{A_0} - F_{B_0}X_B$
B	F_{B_0}	F_B	$F_{B_0}(1-X_B)$
C	–	F_C	$X_BF_{B_0}$
D	–	F_D	$X_BF_{B_0}$
			$F_t = F_{A_0} + F_{B_0}$

  - → thus,

$$\frac{dX_B}{dV} = 7.5\times10^{11}\times \exp\left(\frac{-17940}{T}\right)\frac{(F_{A_0} - X_BF_{B_0})(1-X_B)}{(F_{A_0}+F_{B_0})^2}\left(\frac{P_0}{RT}\right)^2$$

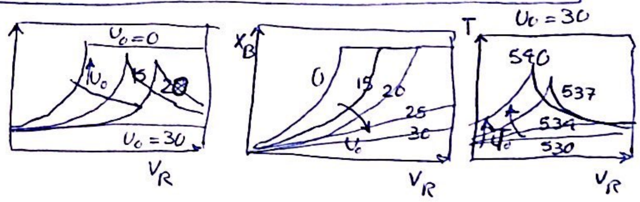
- Ex. 01 solution "EBE"
  - →

$$\frac{dT}{dV} = \frac{\frac{4U_0}{D}(T_a - T) - (\Delta H_{R,B})(-r_B)}{\sum_i F_iC_{P_i}}$$

  - → $\Delta H_{R,B} = \Delta H^o_{R,298} + \int_{298}^{T}(\Delta C_P)dT \Rightarrow \Delta H_{R,B} = \Delta H^o_{R,298} + \Delta C_P(T-298)$
  - → $\sum_i F_iC_{P_i} = (F_{A_0} - X_BF_{B_0})C_{P_A} + F_{B_0}(1-X_B)C_{P,B} + F_{B_0}X_B(C_{P_C} + C_{P_D})$
  - → finally:

$$\frac{dT}{dV} = \frac{\frac{4U_0}{D}(T_0 - T) - [\Delta H^o_{R,298} + \Delta C_P(T-298)]\times 7.5\times10^{11}\times \exp\left(\frac{-17940}{T}\right)\frac{F_{B_0}(1-X_B)(F_{A_0}-X_BF_{B_0})}{(F_{A_0}+F_{B_0})^2}\left(\frac{P_0}{RT}\right)^2}{(F_{A_0} - X_BF_{B_0})C_{P_A} + F_{B_0}(1-X_B)C_{P_B} + F_{B_0}X_B(C_{P_C} + C_{P_D})}$$

  - → numerical solution using Runge-Kutta 4^{th} order with following initial conditions: @ $V_R = 0$; $T = T_0$, $X_B = 0$

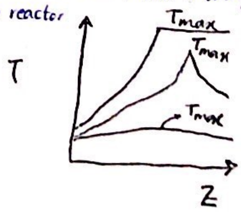


② Parametric Sensitivity of PFRs

- In the previous example for a Non-Isothermal PFR
  - → we saw extreme responses in the T and Concentration profiles resulting from small changes in operating conditions
  - → These types of extreme responses of a PFR occur for highly exothermic rxns when the reactor is operating under certain conditions.
  - → Such behavior is formed parametric sensitivity.
  - → Obviously, the most important problem associated with parametric sensitivity is to determine conditions under which this sensitivity is to be expected and what criteria may be established to ensure its absence.
  - → Such dramatic rise in T may
    - → destroy catalyst which are T-sensitive.
    - → causes fatigue in the reactor construction material.
    - → lead to explosion.

- Accurence of "Hot spots" in PFRs
  - → "EBE" in a PFR: $\frac{dT}{dV} = \frac{4U_0/D}{\dot{m}C_P}(T_a - T) - \frac{(\Delta H_{R,A})(-r_A)}{\dot{m}C_P}$ ①
  - → for a tubular PFR: $dV = \frac{\pi D^2}{4}dz$ ② , where z is the distance along the reactor.
  - → ② in ① $\Rightarrow$ $\frac{dT}{dz} = \frac{\pi DU_0}{\dot{m}C_P}(T_a - T) - \frac{(\Delta H_{R,A})(-r_A)}{\dot{m}C_P}\left(\frac{\pi D^2}{4}\right)$ ③ → describes the variation in rxn T along the length of the reactor
  - → The "Hot-spot" T is defined as the max reactor T.
  - → T_{max} occurs when: $\frac{dT}{dz} = 0$
  - → hence, at the hot-spot T, we have:

$$\underbrace{\frac{4U_0}{D}(T_a - T_{max})}_{\text{heat removed by heat transfer to surroundings at } T_a} = \underbrace{(\Delta H_{R,A})(-r_A)}_{\text{heat generated by the rxn}} \quad ④$$



- To establish some control over sensitivity
  - → we can specify some allowable T_{max} and manipulate heat transfer coefficient U_o and/or reactor wall T (T_a) such that at T_{max}:
    rate of generation of heat $\leq$ rate of removal of heat (5)
  - → suppose at the hot-spot T, T_{max}, the reactor concentration is $C_{A,max}$.
  - → we can rewrite eq. 5 as:
    $$\frac{4U_o}{D}(T_a - T_{max}) = (\Delta H_{R,A})\underbrace{[-r_A(T_{max}, C_{A,max})]}_{\text{rxn rate @ } T_{max} \text{ and corresponding to } C_{A,max}} \quad (6)$$
  - → The problem is $C_{A,max}$ is not known apriori.
  - → To obtain $C_{A,max}$ we must solve the ODEs of energy and material balance.
  - → However, we can make a conservative estimate:
    $$-r_A(T_{max}, C_{A,max}) < -r_A(T_{max}, \underset{\text{reactor inlet concentration}}{C_{A0}}) \quad (7)$$
    - eq. 7 is true for powerlaw kinetics ($-r_A = kC_A^n$)
  - → (6), (7) $\Longrightarrow$ $\frac{4U_o}{D}(T_a - T_{max}) \leq (\Delta H_{R,A})[-r_A(T_{max}, C_{A0})]$ (8)
  - → hence, to avoid parametric sensitivity, we can specify T_{max} and manipulate U_o and/or T_a such that the above inequality holds.
  - → plot
    - → Note that the two curves are obtained by specifying a T_{max} and evaluating $-r_A$.
    - → $-r_A(T_{max}, C_{A0})$ is known since we know C_{A0} and specified T_{max}, but $-r_A(T_{max}, C_{A,max})$ is not known apriori.
    - → The solid straight line's
      - → intercept = T_a
      - → slope = $4U_o/D$
      - → and corresponds to the heat removal
    - → $T_{max,2}$ is the design specified max T based on $-r_A(T_{max}, C_{A0})$ curve.
    - → the actual max T that will be obtained, however, is $T_{max,1}$.