

6. Energy balance on chemical reactors

Most of reactions are not carried out isothermally

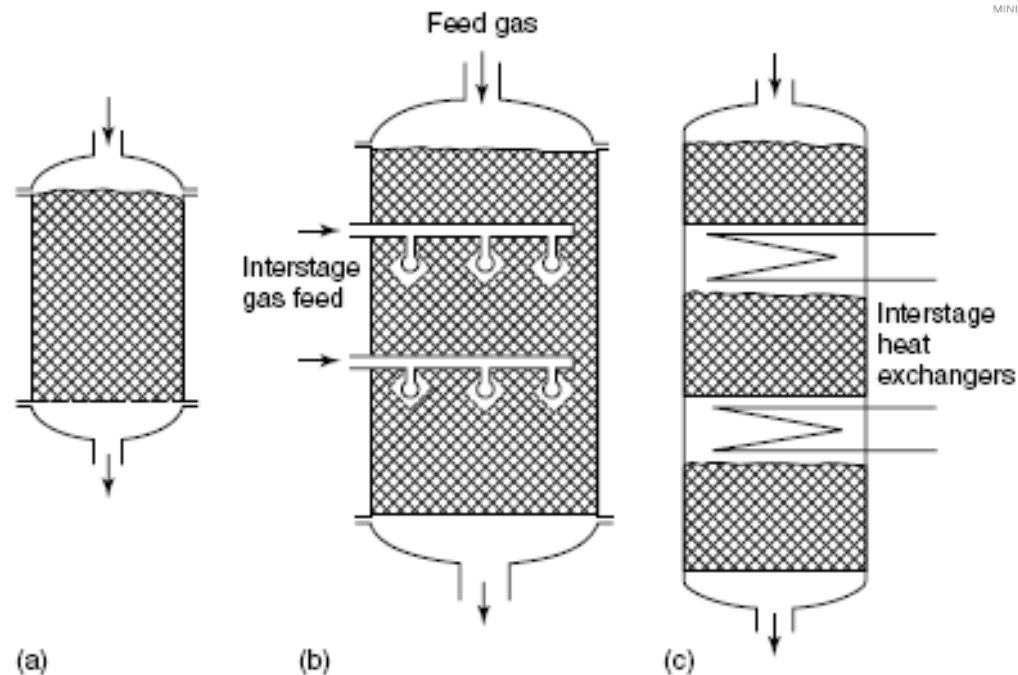


Fig. 12 Development of fixed-bed reactors. (a) Single-bed adiabatic packed-bed reactor; (b) adiabatic reactor with interstage gas feed (ICI concept); (c) multi-bed adiabatic fixed-bed reactor with interstage heat exchange.

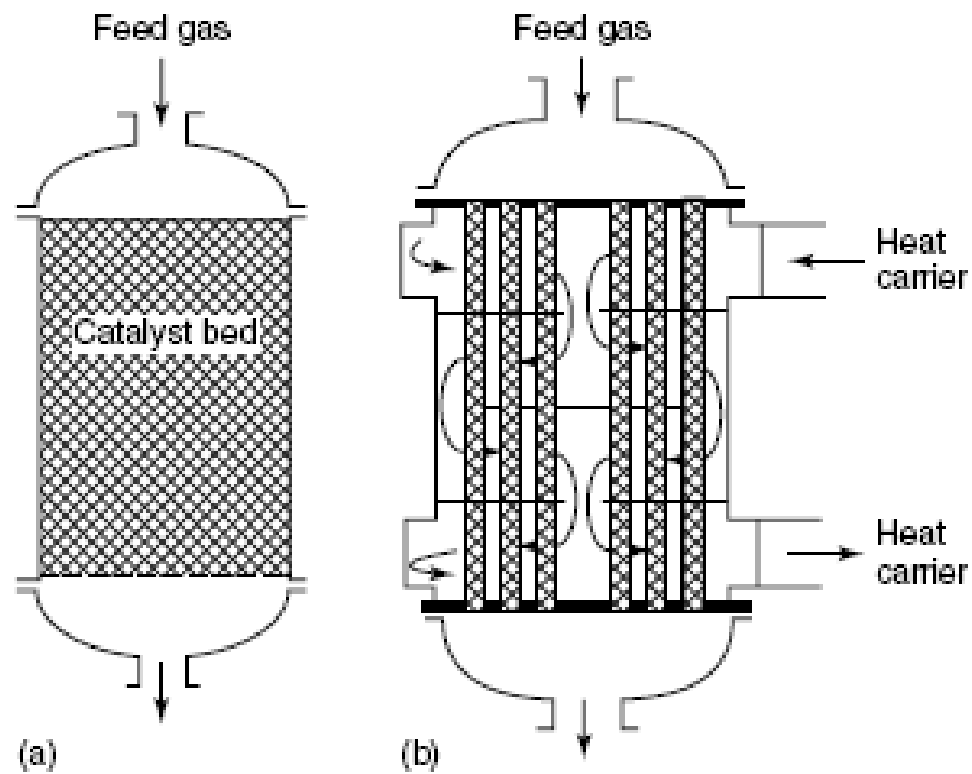


Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.

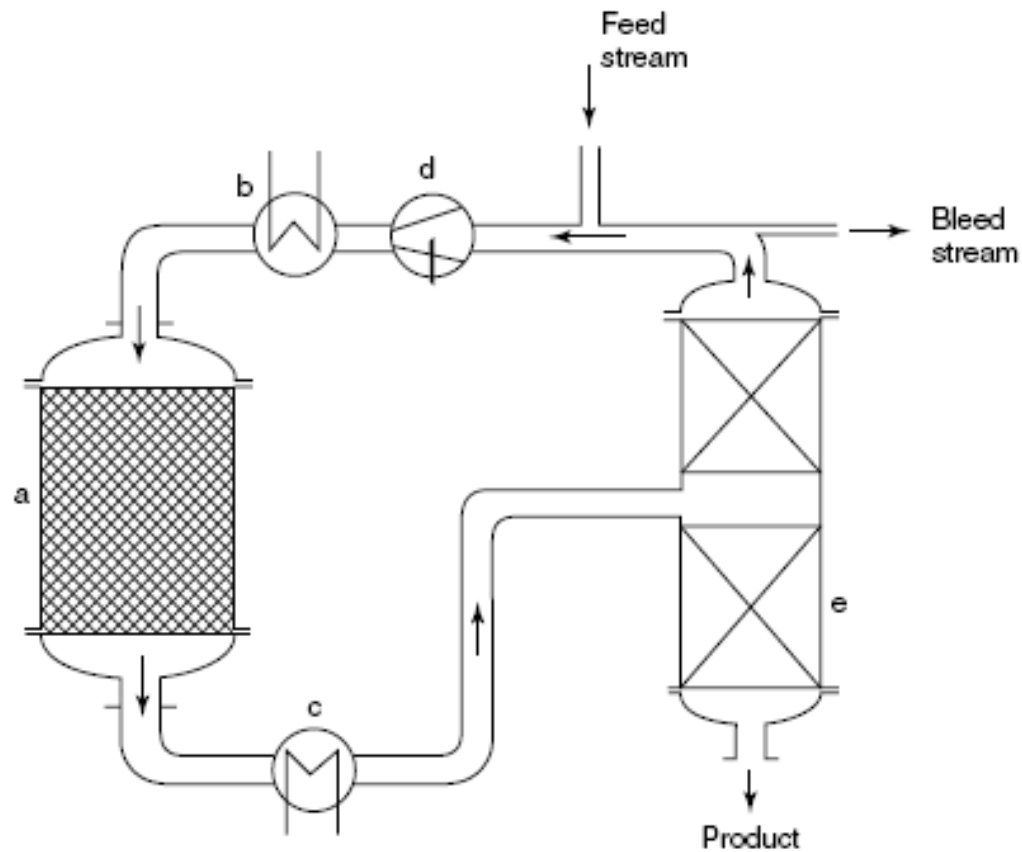
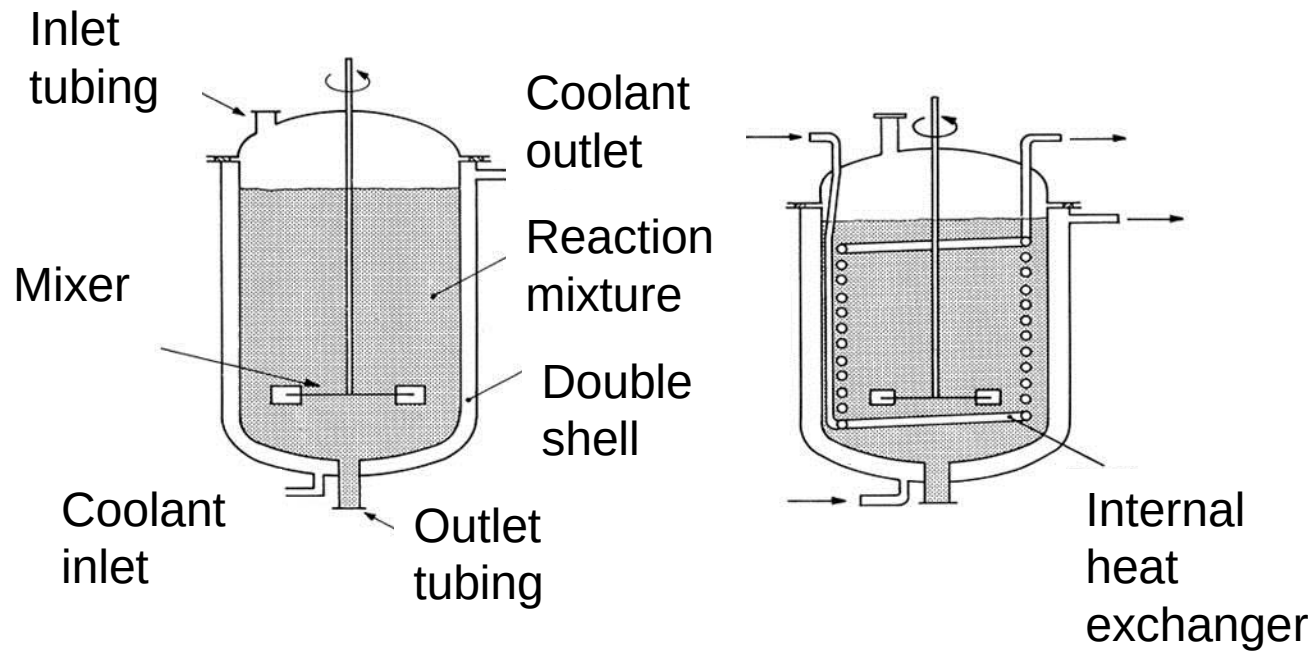


Fig. 2 Reaction cycle for synthesis reactions with incomplete conversion. (a) Fixed-bed reactor; (b) feed preheater; (c) exit cooler; (d) recirculation compressor; (e) separation device.

BATCH or CSTR heated (cooled) reactors



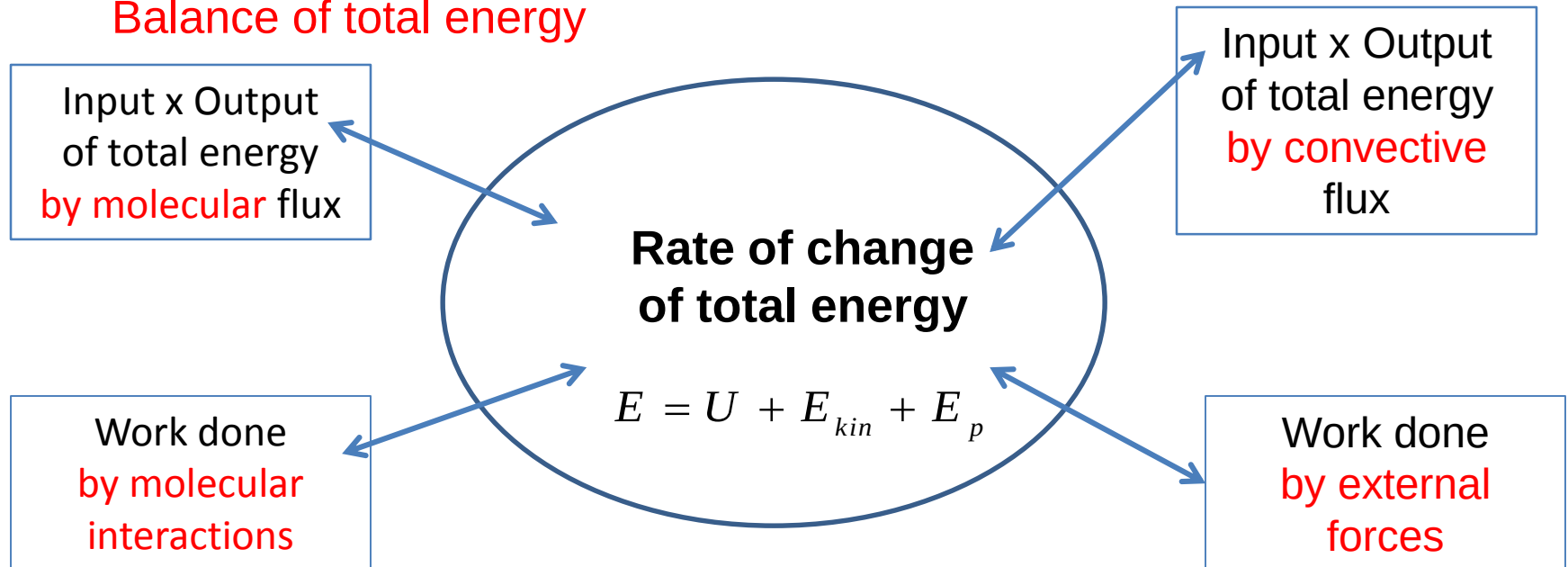
The balance of total energy involves:

Internal energy
mechanical energy (kinetic energy)
potential energy
....

R.B.Bird, W.E.Stewart, E.N.Lightfoot :
Transport Phenomena, 2nd Edition,
J.Wiley&Sons, N.Y. 2007

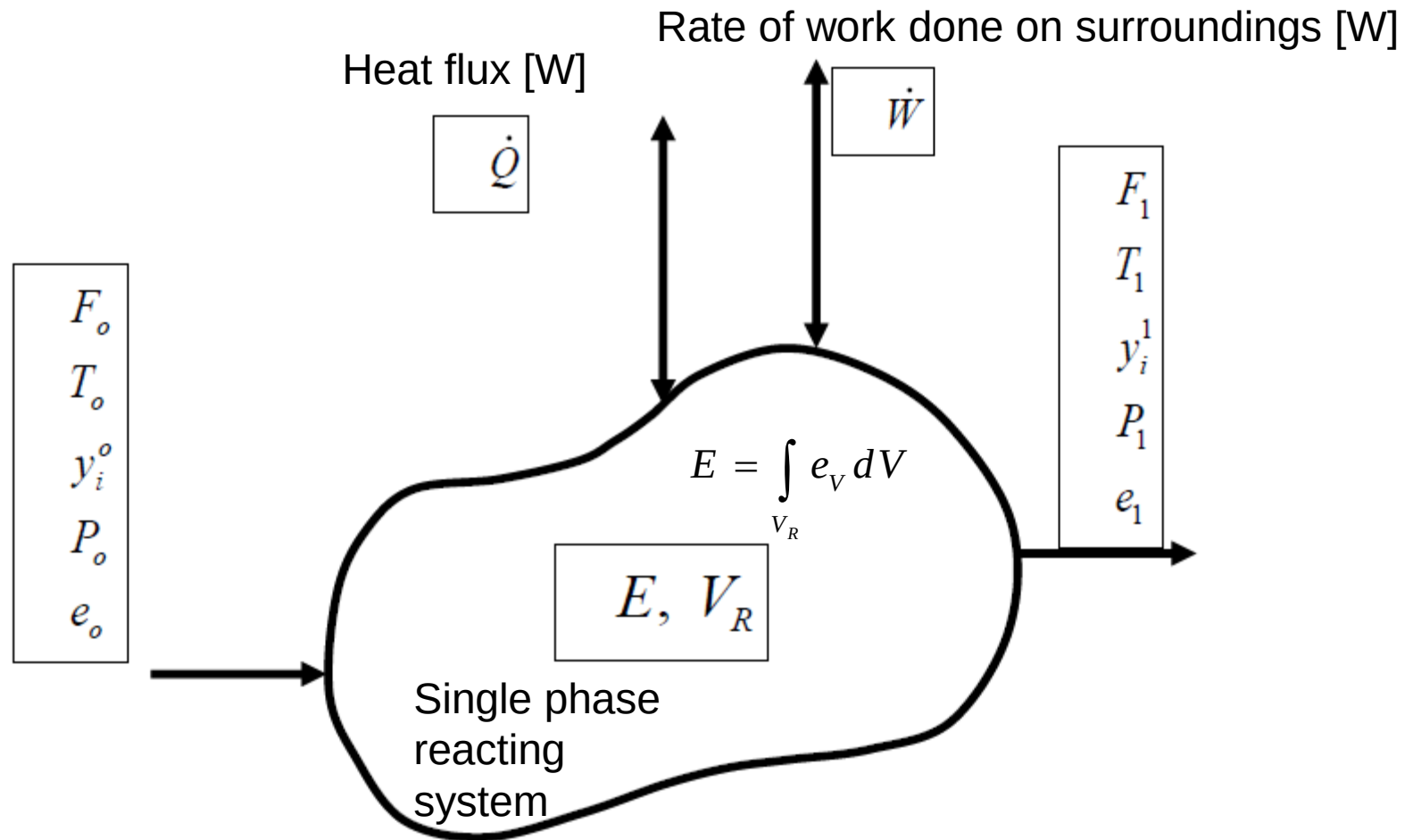
Transformation of various kinds of energy

Balance of total energy



Main reason to study energy balances : assesment of
temperature of reacting system (reactor)

Application of the 1st law of thermodynamics on the open homogeneous reacting system



e_o, e_1 – specific total energy of inlet (outlet) streams [J/mol]

V_R – volume of reaction mixture [m^3]

$$\frac{dE}{dt} = F_o e_o - F_1 e_1 + \dot{Q} + \dot{W}$$

e_o, e_1 – molar energies of inlet and outlet streams [J/mol]

Rate of work $\dot{W}$ done by the reacting system on the surroundings consists of:

- Flow work of inlet stream(s)

$$\dot{V}_o P_o = F_o V_{mo} P_o$$

- Flow work of outlet stream(s)

$$-\dot{V}_1 P_1 = -F_1 V_{m1} P_1$$

- Work provided by stirrer

$$\dot{W}_s$$

- Work done by volume change

$$-P \frac{dV_R}{dt}$$

- Work done by electric, magnetic fields

$$\dot{W}_f$$

$$\frac{dE}{dt} = F_o (e_o + V_{mo} P_o) - F_1 (e_1 + V_{m1} P_1) + \dot{Q} - P \frac{dV_R}{dt} + \dot{W}_s + \dot{W}_f$$

Neglecting potential and kinetic energies ($E \cong U$), we have

$$\frac{dU}{dt} = F_o h_{mo} - F_1 h_{m1} + \dot{Q} - P \frac{dV_R}{dt} + \dot{W}_s + \dot{W}_f$$

h_{mo}, h_{m1} – molar enthalpies of inlet and outlet streams [J/mol]

If $\dot{W}_s \cong 0, \dot{W}_f \cong 0$

$$\frac{dU}{dt} = F_o h_{mo} - F_1 h_{m1} + \dot{Q} - P \frac{dV_R}{dt}$$

From enthalpy definition

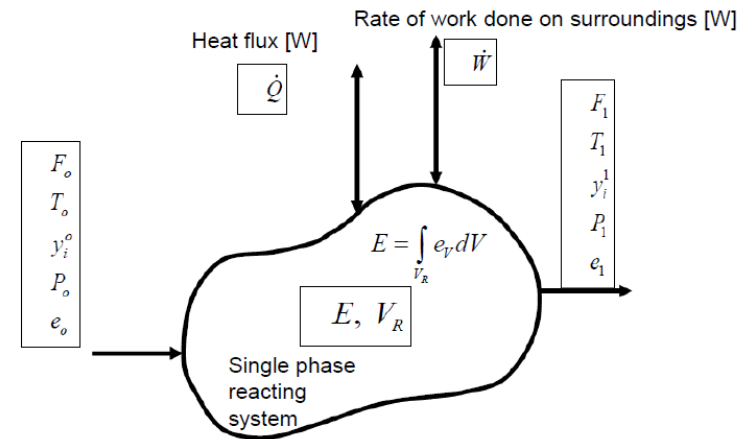
$$\frac{dH}{dt} = \frac{dU}{dt} + V_R \frac{dP}{dt} + P \frac{dV_R}{dt} \longrightarrow \frac{dH}{dt} = V_R \frac{dP}{dt} + F_o h_{mo} - F_1 h_{m1} + \dot{Q}$$

Introducing partial molar enthalpies of species

$$F_o h_{mo} = \sum_{i=1}^N F_i^o \bar{H}_i^o$$

$$F_1 h_{m1} = \sum_{i=1}^N F_i \bar{H}_i$$

We have finally



$$\frac{dH}{dt} = V_R \frac{dP}{dt} + \sum_{i=1}^N F_i^o \bar{H}_i^o - \sum_{i=1}^N F_i \bar{H}_i + \dot{Q}$$

BATCH reactor

$$\frac{dH}{dt} = V_R \frac{dP}{dt} + \dot{Q}$$

Enthalpy is a function of temperature, pressure and composition

Total heat capacity [J/K]

Partial molar enthalpy [J/mol]

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P,n} dT + \left(\frac{\partial H}{\partial P} \right)_{T,n_j} dP + \sum_{i=1}^N \left(\frac{\partial H}{\partial n_i} \right)_{T,P,n_{j \neq i}} dn_i$$

$$= C_P dT + \left(\frac{\partial H}{\partial P} \right)_{T,n_j} dP + \sum_{i=1}^N \bar{H}_i dn_i = \rho_m V_R c_P dT + \left(\frac{\partial H}{\partial P} \right)_{T,n_j} dP + \sum_{i=1}^N \bar{H}_i dn_i$$

Molar density [mol/m³] Molar heat capacity [J/mol/K]

We know that (from thermodynamics)

$$\left(\frac{\partial H}{\partial P} \right)_{T, n_j} = \left[V_R - T \left(\frac{\partial V_R}{\partial T} \right)_{P, n_j} \right] = V_R (1 - \alpha_p T)$$

where the coefficient of isobaric expansion is defined as

$$\alpha_p = \frac{1}{V_R} \left(\frac{\partial V_R}{\partial T} \right)_{P, n_j}$$

and we obtain

$$\frac{dH}{dt} = \rho_m c_p V_R \frac{dT}{dt} + V_R (1 - \alpha_p T) \frac{dP}{dt} + \sum_{i=1}^N \bar{H}_i \frac{dn_i}{dt}$$

Finally by substitution of $\frac{dn_i}{dt}$ in the energy balance of the batch reactor

$$\rho_m c_p V_R \frac{dT}{dt} - \alpha_p V_R T \frac{dP}{dt} + \sum_{i=1}^N \bar{H}_i \frac{dn_i}{dt} = \dot{Q} \quad \frac{dn_i}{dt} = V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k}$$

Using definition of the enthalpy of k-th reaction

$$\Delta_r H_k = \sum_{i=1}^N \nu_{ki} \bar{H}_i$$

we have

$$\rho_m c_P V_R \frac{dT}{dt} = \alpha_p V_R T \frac{dP}{dt} + V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \dot{Q}$$

Isobaric reactor ($\frac{dP}{dt} = 0$)

$$\rho_m c_P V_R \frac{dT}{dt} = V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \dot{Q}$$

$V_R = f(t) \rightarrow$ we need state equation !

Homework 8: Energy balance of ideal gas isobaric batch reactor

Isochoric reactor ($\frac{dV_R}{dt} = 0$)

$$\rho_m V_R c_V \frac{dT}{dt} = V_R \sum_{k=1}^{NR} \left[\left(-\Delta_r H_k \right) + T \frac{\alpha_p}{\kappa_T} \Delta \bar{V}_k \right] r_{V,k} + \dot{Q}$$

$$P = f(t)$$

the coefficient of isobaric expansion

the coefficient of isothermal compressibility

$$\alpha_p = \frac{1}{V_R} \left(\frac{\partial V_R}{\partial T} \right)_{P, n_j}$$

$$\kappa_T = -\frac{1}{V_R} \left(\frac{\partial V_R}{\partial P} \right)_T$$

the volume variation due to k-th chemical reaction

$$\Delta \bar{V}_k = \sum_{i=1}^N \nu_{ki} \bar{V}_i, \quad \text{where } \bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}} \text{ is the partial molar volume of species } i$$

the specific heat capacity at **constant volume**

$$C_V = C_P - T \left(\frac{\partial P}{\partial T} \right)_{V, n_j} \left(\frac{\partial V_R}{\partial T} \right)_{P, n_j} = C_P - T V_R \left(\frac{\partial P}{\partial T} \right)_{V, n_j} \alpha_p = C_P - T V_R \frac{\alpha_p^2}{\kappa_T}$$

Variation of the pressure can be derived from total differential of volume

$$\frac{dP}{dt} = - \frac{\left(\left(\frac{\partial V_R}{\partial T} \right)_{P, n_j} \frac{dT}{dt} + \sum_{i=1}^N \bar{V}_i \frac{dn_i}{dt} \right)}{\left(\frac{\partial V_R}{\partial P} \right)_{T, n_j}} = \frac{\alpha_p}{\kappa_T} \frac{dT}{dt} + \frac{1}{V_R \kappa_T} \sum_{i=1}^N \bar{V}_i \frac{dn_i}{dt}$$

Homework 9: Energy balance of ideal gas isochoric batch reactor

Summary of energy balance of BATCH reactor

$\frac{dP}{dt} = 0$	$\rho_m c_p V_R \frac{dT}{dt} = V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \dot{Q}$ $V_R = f(t)$
$\frac{dV_R}{dt} = 0$	$\rho_m V_R c_V \frac{dT}{dt} = V_R \sum_{k=1}^{NR} \left[(-\Delta_r H_k) + T \frac{\alpha_p}{\kappa_T} \Delta \bar{V}_k \right] r_{V,k} + \dot{Q}$ $P = f(t)$

If $\alpha_p \cong 0, c_p \cong c_V$

liquid (condensed) systems

$$\underbrace{\rho_m c_p V_R \frac{dT}{dt}}_{\text{Rate of change of reaction mixture enthalpy}} = \underbrace{V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k}}_{\text{Rate of heat generation by chemical reactions}} + \underbrace{\dot{Q}}_{\text{Rate of heat loss (input)}}$$

Heat flux : $\dot{Q} = \omega S_H (T_e - T)$

ω – the overall (global) heat transfer coefficient [$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$]

S_H – the heat exchange area [m^2]

T_e – temperature of external cooling (heating) fluid

Limiting cases

Isothermal reactor	$\rho_m c_p V_R \frac{dT}{dt} = 0 \Rightarrow V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} = \dot{Q}$
Adiabatic reactor	$\dot{Q} = 0 \Rightarrow \rho_m c_p V_R \frac{dT}{dt} = V_R \sum_{k=1}^{NR} [(-\Delta_r H_k) r_{V,k}]$

Example

Adiabatic reactor with 1 reaction, constant heat capacities

Energy balance on adiabatic BATCH reactor

$$\rho_m c_p V_R \frac{dT}{dt} = V_R (-\Delta_r H) r_V$$

Molar balance of key component

$$\frac{dc_j}{dt} = -c_j^o \frac{dX_j}{dt} = \nu_j r_V$$

$$\rho_m V_R = n, c_p = \sum_{i=1}^N y_i c_{pi}$$

$$\rho_m V_R c_p = n \sum_{i=1}^N y_i c_{pi} = \sum_{i=1}^N n_i c_{pi} = \sum_{i=1}^N \left(n_i^o - \frac{\nu_i}{\nu_j} n_j^o X_j \right) c_{pi} =$$

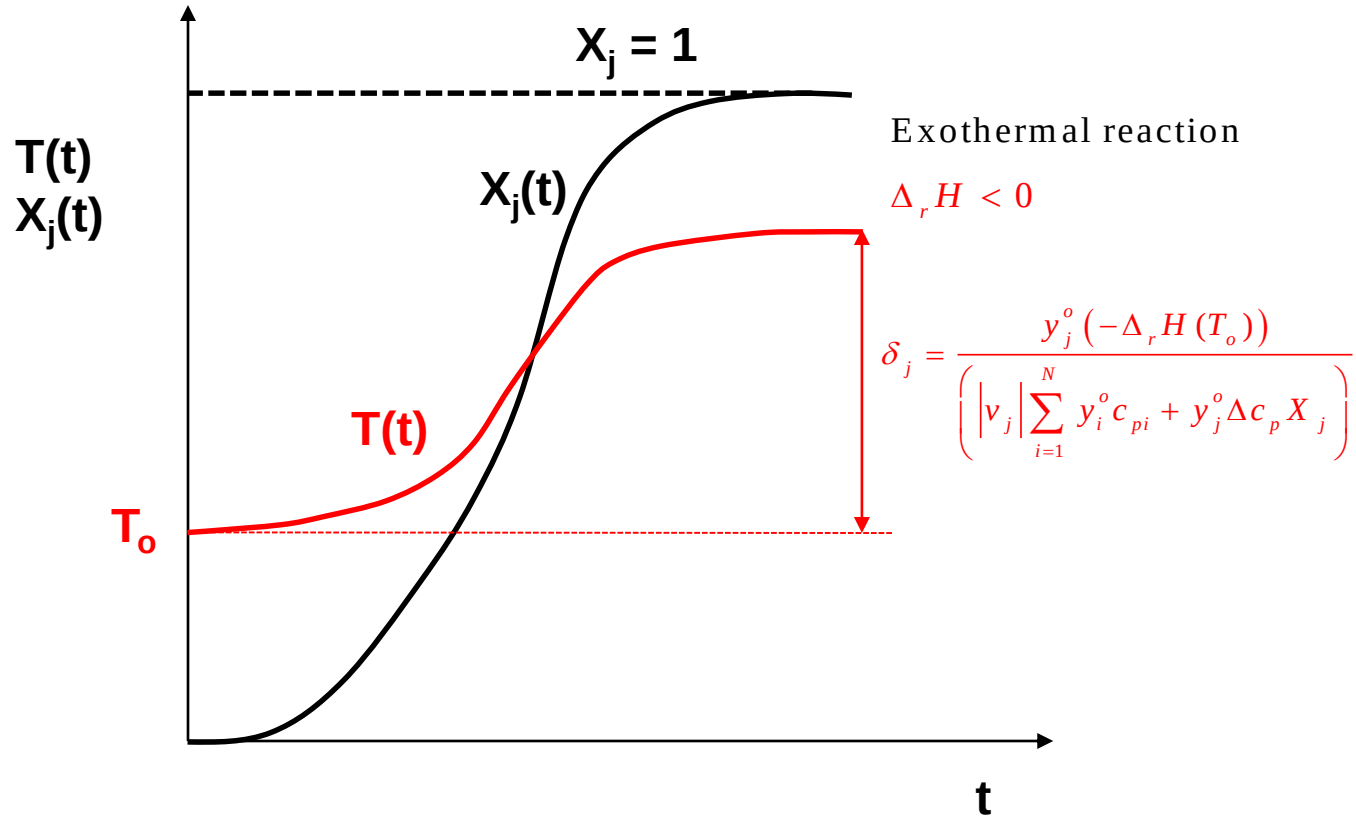
$$= \sum_{i=1}^N (n_i^o c_{pi}) - \frac{n_j^o X_j}{\nu_j} \sum_{i=1}^N (\nu_i c_{pi}) = \sum_{i=1}^N (n_i^o c_{pi}) + \frac{n_j^o X_j}{|\nu_j|} \Delta c_p$$

Assuming that $c_{pi} = \text{const} \Rightarrow \Delta c_p = \text{const}$

$$T = T_o + \frac{y_j^o (-\Delta_r H(T_o)) X_j}{\left(|\nu_j| \sum_{i=1}^N y_i^o c_{pi} + y_j^o \Delta c_p X_j \right)} = T_o + \delta_j X_j$$

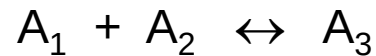
$$\delta_j = \frac{y_j^o (-\Delta_r H(T_o))}{\left(|\nu_j| \sum_{i=1}^N y_i^o c_{pi} + y_j^o \Delta c_p X_j \right)} \quad \text{the adiabatic rise of temperature}$$

Trajectories of $T(t)$ and $X_j(t)$



Homework 10

The reversible reaction



is carried out adiabatically in a constant-volume BATCH reactor. The kinetic equation is

$$r = k_f c_1^{1/2} c_2^{1/2} - k_b c_3$$

$$k_f(373 \text{ K}) = 2 \times 10^{-3} \text{ s}^{-1} \quad E_1 = 100 \text{ kJ/mol}$$

$$k_b(373 \text{ K}) = 3 \times 10^{-5} \text{ s}^{-1} \quad E_2 = 150 \text{ kJ/mol}$$

Initial conditions and thermodynamic data

$$c_1^o = 0.1 \text{ mol/dm}^3 \quad c_{p1} = 25 \text{ J/mol/K}$$

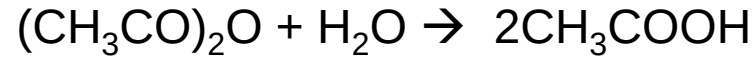
$$c_2^o = 0.125 \text{ mol/dm}^3 \quad c_{p2} = 25 \text{ J/mol/K}$$

$$\Delta_r H_{298}^o = -40 \text{ kJ/mol} \quad c_{p3} = 40 \text{ J/mol/K} \quad T^o = 373 \text{ K}$$

Calculate $X_1(t)$, $T(t)$.

Example

Acetic anhydride reacts with water



in a BATCH reactor of constant volume of 100 l. Kinetics of reaction is given by

$$r_v = 2.14 \times 10^7 e^{-\frac{46500}{RT}} c_1 \text{ mol.m}^{-3}.\text{min}^{-1}$$

Data

$$c_1^o = 0.3 \text{ mol.l}^{-1}, c_{pM} = 3.8 \text{ kJ.kg}^{-1}.\text{K}^{-1}, \Delta H_r = -209 \text{ kJ.mol}^{-1}, \rho = 1070 \text{ kg.m}^{-3}$$

$$\omega.S_H = 200 \text{ W.K}^{-1} \quad T_e = T^o = 300 \text{ K}, \Delta c_p = 0, c_{pM} = \sum_i w_i^o c_{pMi}, c_{pMi} = \frac{c_{pi}}{M_i}$$

w_i^o – initial mass fractions, c_{pMi} – mass heat capacities ($\text{kJ.kg}^{-1}.\text{K}^{-1}$), M_i – molar weight (kg.mol^{-1})

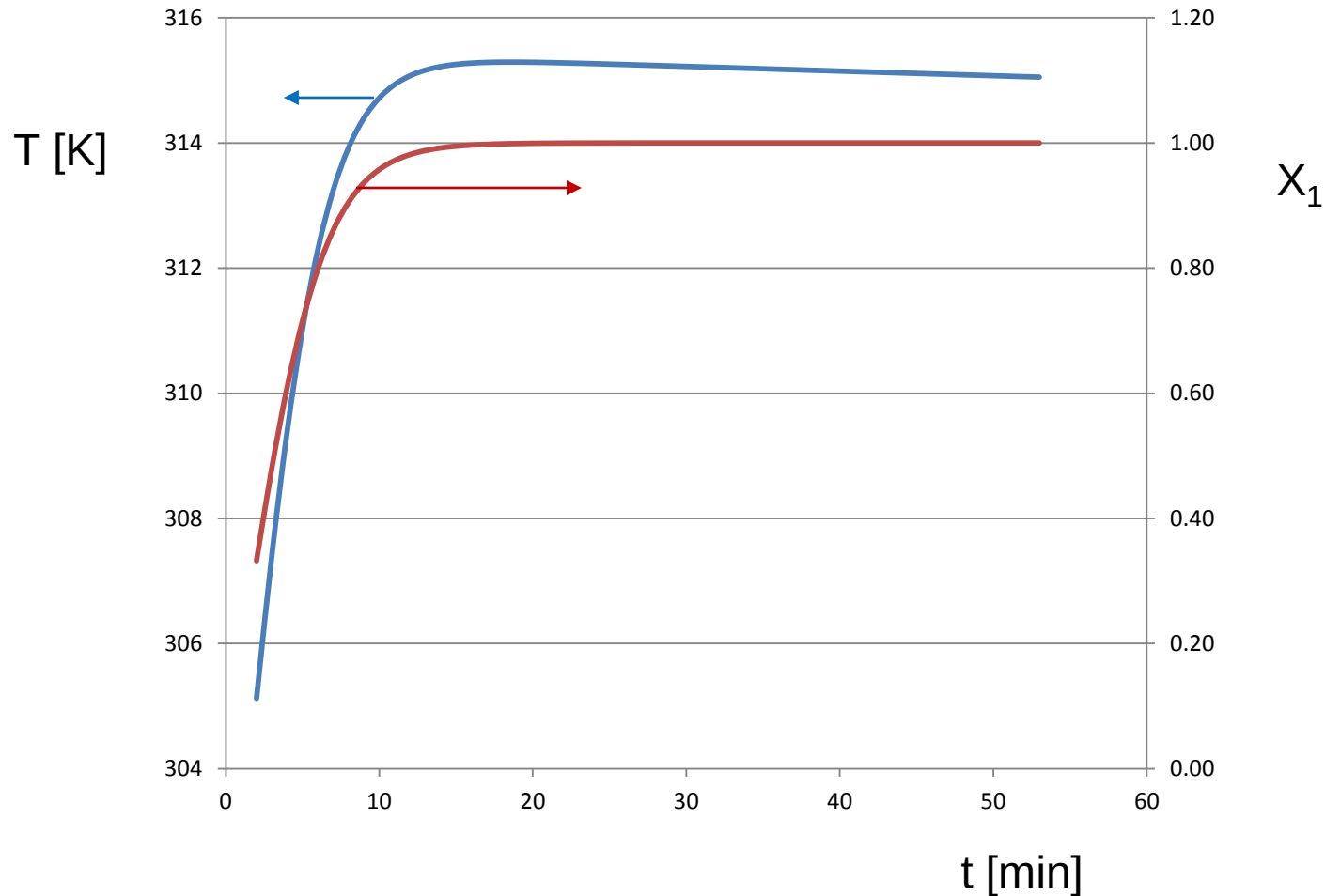
$$R = 8.31446 \text{ J.mol}^{-1}.\text{K}^{-1}$$

In neglecting variation of heat capacities with temperature, calculate $T(t)$ and $X_1(t)$ for an non-adiabatic and adiabatic case.

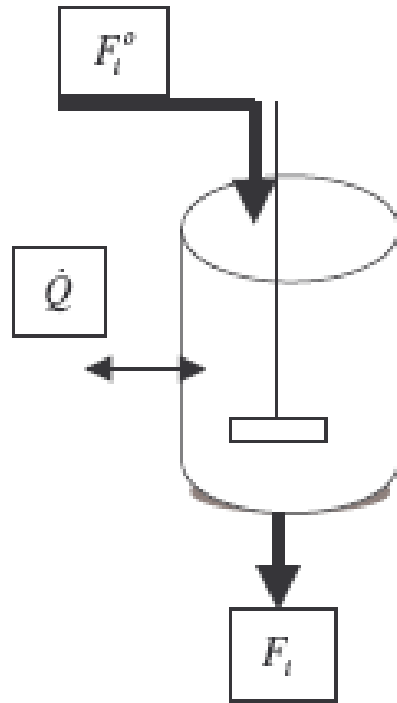
By numerical integration we get

$$\frac{dT}{dt} = \frac{1}{(1070 \times 3.8E3 \times 0.1)} \left(0.1 \times 209E3 \times 2.14E7 \times \exp \left[-\frac{46500}{(8.31446 \times T)} \right] 300 \times (1 - X_1) + 200 \times (300 - T) \right)$$

$$\frac{dX_1}{dt} = 2.14E7 \times \exp \left[-\frac{46500}{(8.31446 \times T)} \right] (1 - X_1)$$



Continuous (perfectly) stirred reactor (CSTR)



Energy balance on CSTR

$$\frac{dH}{dt} = V_R \frac{dP}{dt} + \sum_{i=1}^N F_i^o \bar{H}_i^o - \sum_{i=1}^N F_i \bar{H}_i + \dot{Q}$$

Total differential of enthalpy

$$\begin{aligned} \frac{dH}{dt} &= \rho_m c_p V_R \frac{dT}{dt} + V_R (1 - \alpha_p T) \frac{dP}{dt} + \sum_{i=1}^N \bar{H}_i \frac{dn_i}{dt} = \\ &= V_R \frac{dP}{dt} + \sum_{i=1}^N F_i^o \bar{H}_i^o - \sum_{i=1}^N F_i \bar{H}_i + \dot{Q} \end{aligned}$$

Molar balance on CSTR

$$\frac{dn_i}{dt} = F_i^o - F_i + V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k}, \quad i = 1, N$$

We get

$$\rho_m c_P V_R \frac{dT}{dt} - \alpha_p T V_R \frac{dP}{dt} + \sum_{i=1}^N \bar{H}_i \left[F_i^o - F_i + V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \right] =$$

$$= \sum_{i=1}^N F_i^o \bar{H}_i^o - \sum_{i=1}^N F_i \bar{H}_i + \dot{Q}$$

Enthalpy change for k-th reaction

$$\Delta_r H_k = \sum_{i=1}^N \nu_{ki} \bar{H}_i$$

$$\rho_m c_P V_R \frac{dT}{dt} - V_R \alpha_p T \frac{dP}{dt} + V_R \sum_{k=1}^{NR} (\Delta_r H_k) r_{V,k} =$$

$$= \sum_{i=1}^N F_i^o (\bar{H}_i^o - \bar{H}_i) + \dot{Q}$$

$$\frac{dP}{dt} = 0$$

The CSTR usually works at constant pressure (no pressure drop)

$$\rho_m c_P V_R \frac{dT}{dt} = V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \sum_{i=1}^N F_i^o (\bar{H}_i^o - \bar{H}_i) + \dot{Q}$$

$$\dot{Q} = \omega S_T (T_m - T)$$

Steady state

$$\frac{dT}{dt} = \frac{dn_i}{dt} = 0$$

$$V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \sum_{i=1}^N F_i^o (\bar{H}_i^o - \bar{H}_i) + \dot{Q} = 0$$

Assuming ideal mixture, i.e. $\bar{H}_i = H_i$, we have

$$\bar{H}_i^o - \bar{H}_i = H_i^o - H_i = - \int_{T_o}^T c_{pi} dT$$

$$\Delta_r H_k = \Delta_r H_k^o + \int_{T_o}^T (\Delta c_p)_k dT$$

$$(\Delta c_p)_k = \sum_{i=1}^N \nu_{ki} c_{pi}$$

Molar and enthalpy
balances give
N+1 unknown
variables T, F_i

$$V_R \sum_{k=1}^{NR} - \left(\Delta_r H_k^o + \int_{T_o}^T (\Delta c_p)_k dT \right) r_{V,k} - \sum_{i=1}^N F_i^o \int_{T_o}^T c_{pi} dT + \dot{Q} = 0$$

$$F_i^o - F_i + V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k} = 0, \quad i = 1, N$$

N+1 unknown variables in N+1 non linear algebraic equations

$$G_i (T, F_1, F_2, \dots, F_N) = 0, \quad i = 1, N + 1$$

Issues:

- multiple solutions
- slow convergence (divergence)

Example

Adiabatic CSTR with 1 reaction, constant heat capacities

$$V_R \left(-\Delta_r H^\circ - \Delta c_p (T - T^\circ) \right) r_V = \sum_{i=1}^N F_i^\circ c_{pi} (T - T^\circ) = F^\circ (T - T^\circ) \sum_{i=1}^N y_i^\circ c_{pi}$$

$$F_j^\circ X_j + V_R \nu_j r_V = 0 \Rightarrow r_V = \frac{F_j^\circ X_j}{V_R |\nu_j|}$$

$$\left(-\Delta_r H^\circ - \Delta c_p (T - T^\circ) \right) \frac{y_j^\circ X_j}{|\nu_j|} = (T - T^\circ) \sum_{i=1}^N y_i^\circ c_{pi}$$

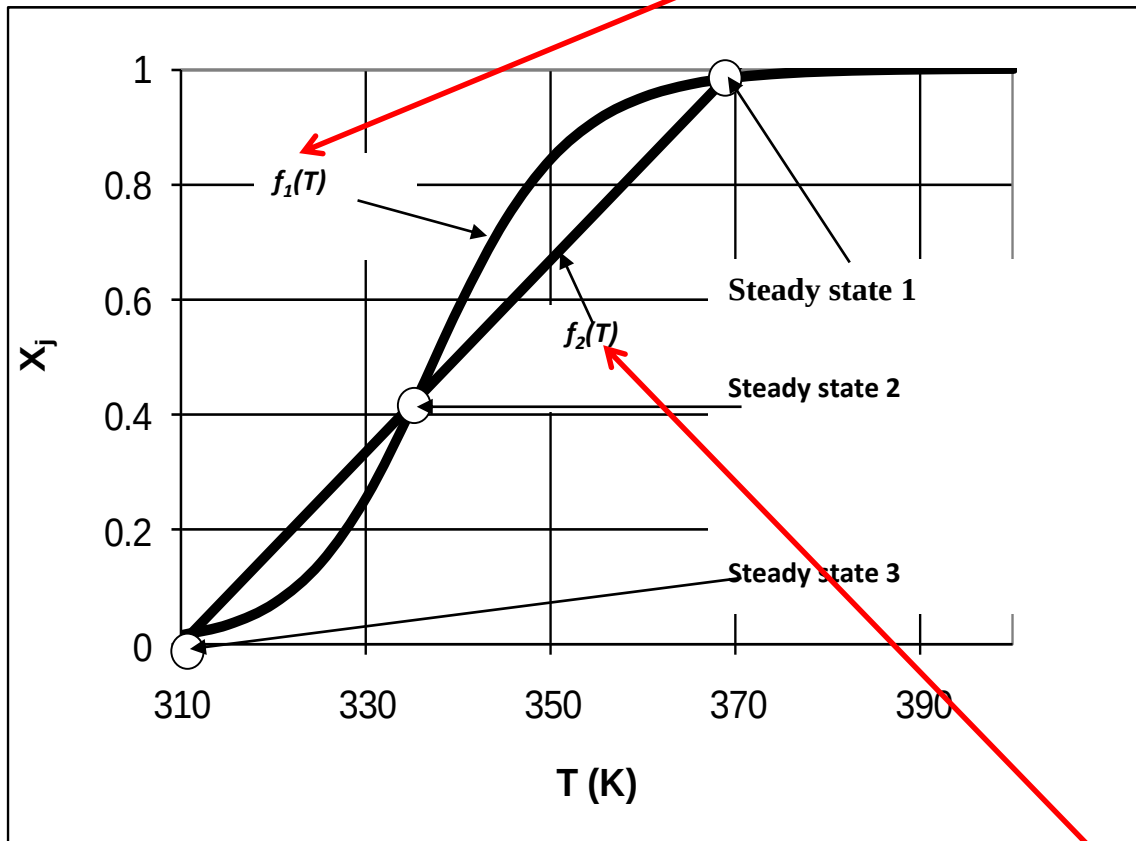
2 nonlinear algebraic equations for unknown T and X_j

$$T = T^\circ + \frac{(-\Delta_r H^\circ) y_j^\circ X_j}{|\nu_j| \sum_{i=1}^N y_i^\circ c_{pi} + \Delta c_p y_j^\circ X_j} =$$

$$= T^\circ + \delta_j X_j \quad \text{cf. adiabatic const.-volume BATCH}$$

Multiple steady states of adiabatic CSTR (exothermal reaction)

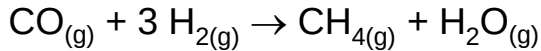
$$F_j^o X_j + v_j r_V(X_j, T) V_R = 0 \Rightarrow X_j = f_1(T)$$



$$T = T_o + \delta_j X_j \Rightarrow X_j = f_2(T)$$

Example

You are to consider an irreversible gas-phase reaction in an adiabatic CSTR at constant pressure (101 kPa). The gas phase reaction is:



$$r_v = k c_{\text{CO}}$$

$$k = 0.001 \exp\left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right] \text{ min}^{-1}$$

$$E_a = 10 \text{ kcal/mol}$$

The feed to the CSTR consists of CO and H₂ at the following (stoichiometric) concentrations:

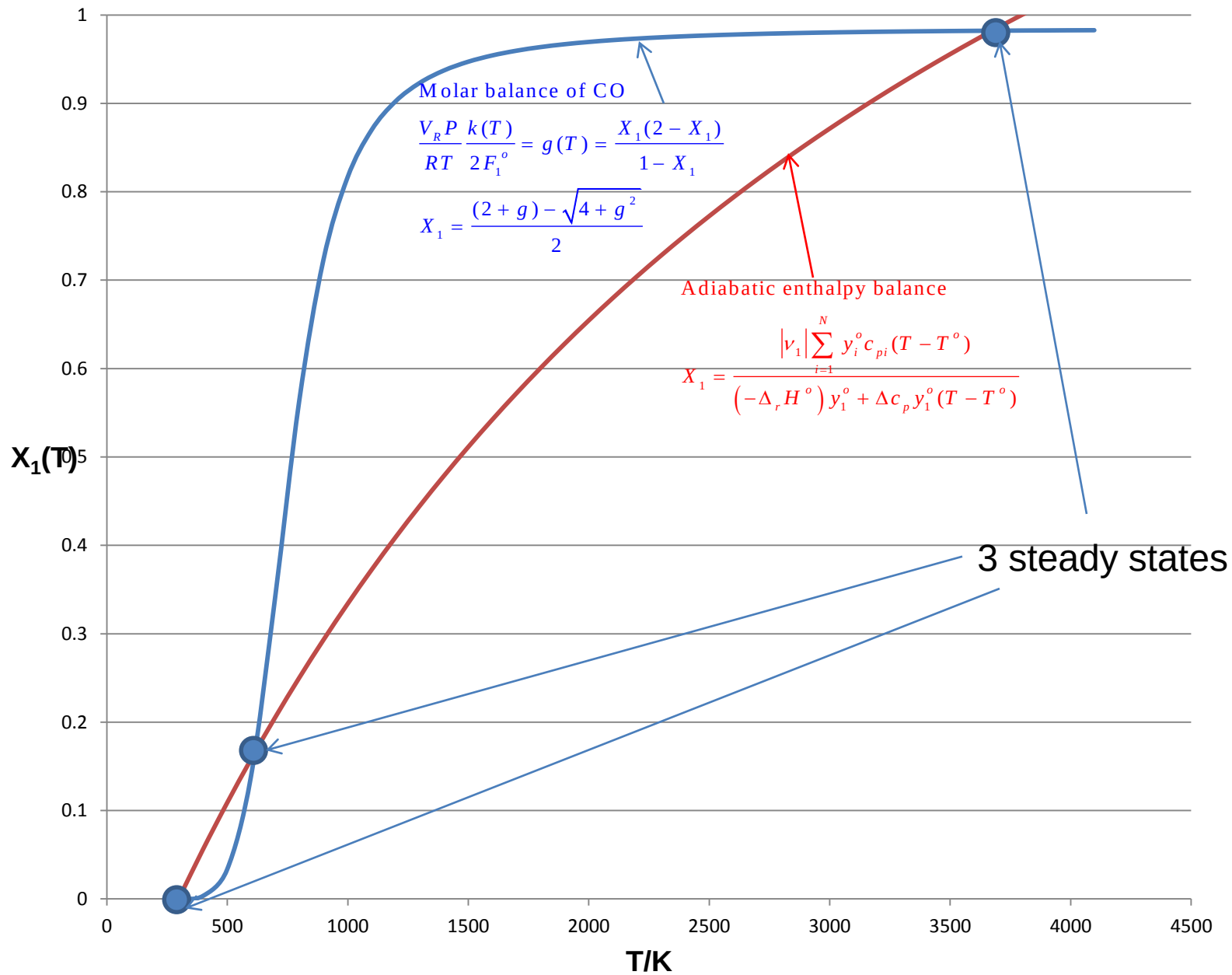
$$C_{\text{CO}}(\text{in}) = 0.0102 \text{ mol/liter} \quad C_{\text{H}_2}(\text{in}) = 0.0306 \text{ mol/liter}$$

The heat of reaction at 298 K is equal to -49.0 kcal/mol.

The heat capacities of CO, H₂, CH₄ and H₂O are all constant and are equal to 7 cal/mol/K.

The temperature of the feed stream is equal to 298 K, the pressure is equal to 101 kPa, the volumetric flow rate of feed is 8 liter/min and volume of reactor is 0.5 l. The gas mixture behaves as ideal gas.

- Use the energy and molar balance to calculate the CO conversion and temperature of the effluent stream from the adiabatic CSTR.
- Calculate the composition in molar fraction of the outlet stream.
- Calculate the volume of the adiabatic CSTR required to achieve the desired CO fractional conversion equal to 0.99.



Remarks:

- Unrealistic temperature of the 3rd steady state → backward reaction will occur
- The 2nd steady state is unstable → careful temperature control has to be used
- The dynamic behavior of reactor should be studied

Homework 11

Determine steady states of adiabatic CSTR in which the exothermal liquid state reaction takes place



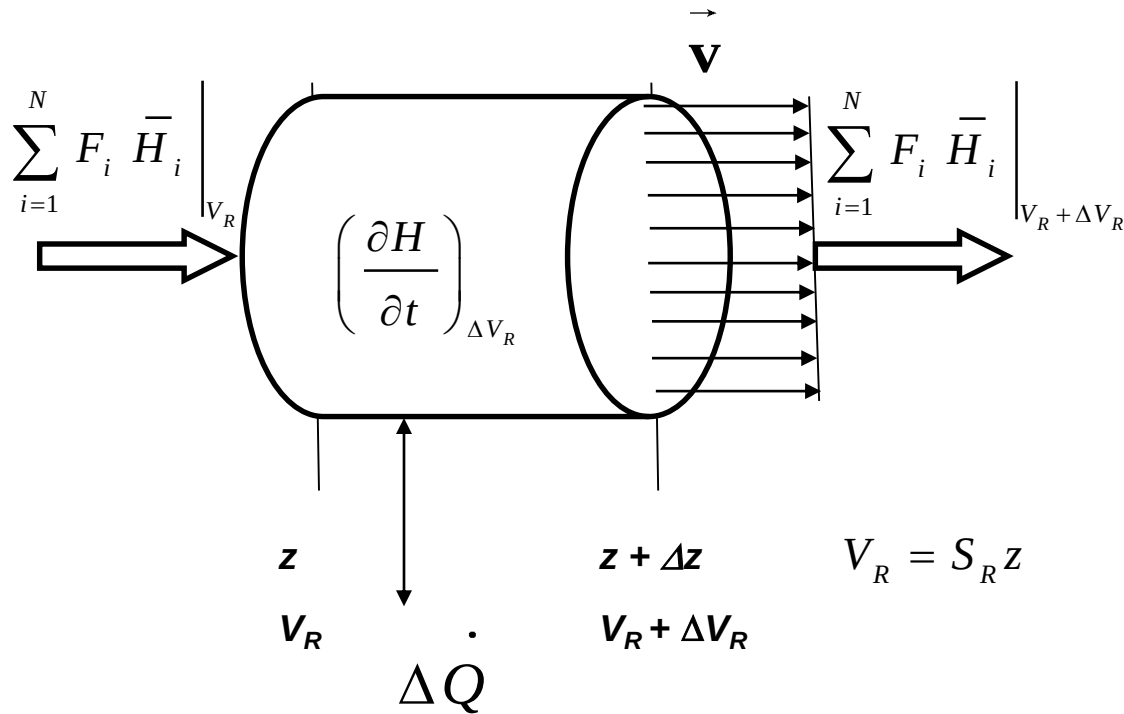
Reaction rate:

$$r_V = A \cdot \exp(-E/RT) \cdot c_{A1} \quad (\text{kmol/m}^3/\text{s})$$

Data

$A = 5.10^{17} \text{ s}^{-1}$	$E = 132.3 \text{ kJ/mol}$
$V_R = 2 \text{ m}^3$	$T^o = 310 \text{ K}$
$\rho = 800 \text{ kg.m}^{-3}$	$c_{A1}^o = 2 \text{ kmol / m}^3$
$\dot{V}^o = 3.33 \text{ l/s}$	$\bar{C}_p^o = 4.19 \text{ kJ.kg}^{-1} \cdot \text{K}^{-1}$
$\Delta H_{r,298} = -100 \text{ kJ / mol}$	

Balance of enthalpy on Plug Flow Reactor (PFR)



$$\left(\frac{\partial H}{\partial t} \right)_{\Delta V_R} = \Delta V_R \frac{dP}{dt} + \sum_{i=1}^N F_i \bar{H}_i \Big|_{V_R} - \sum_{i=1}^N F_i \bar{H}_i \Big|_{V_R + \Delta V_R} + \Delta \dot{Q}$$

in the steady state

$$0 = \sum_{i=1}^N F_i \bar{H}_i \Big|_{V_R} - \sum_{i=1}^N F_i \bar{H}_i \Big|_{V_R + \Delta V_R} + \Delta \dot{Q} \Rightarrow \frac{d}{dV_R} \left(\sum_{i=1}^N F_i \bar{H}_i \right) = \frac{d\dot{Q}}{dV_R}$$

ideal mixture $\Rightarrow \bar{H}_i(T, P, \text{composition}) = h_i(T)$

$$\sum_{i=1}^N \left(\frac{dF_i}{dV_R} h_i(T) + F_i \frac{dh_i(T)}{dV_R} \right) = \sum_{i=1}^N \left(\sum_{k=1}^{NR} \nu_{ki} r_{V,k} h_i(T) + F_i \frac{dh_i(T)}{dT} \frac{dT}{dV_R} \right) =$$

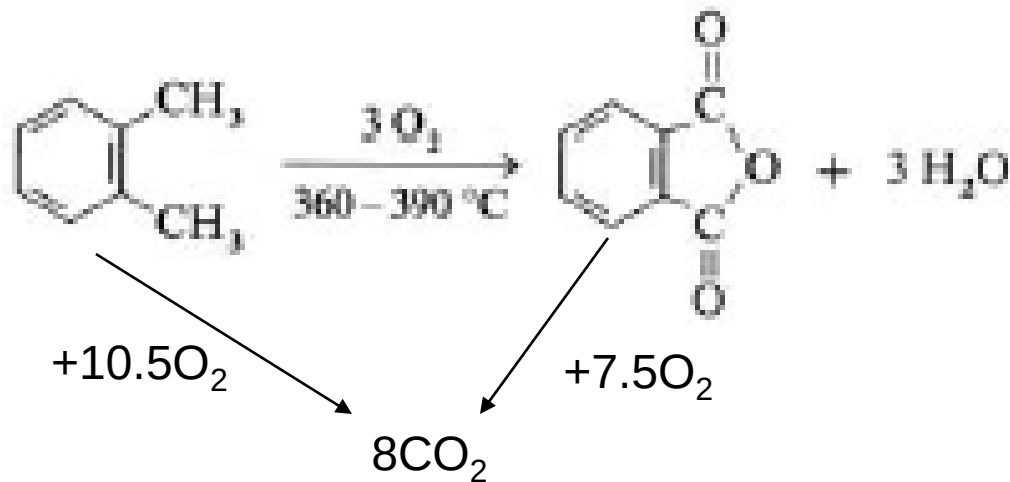
$$= \sum_{k=1}^{NR} \Delta_r H_k r_{V,k} + \frac{dT}{dV_R} \sum_{i=1}^N F_i c_{pi} = \frac{d\dot{Q}}{dV_R}$$

$$\frac{dF_i}{dV_R} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \quad \sum_{i=1}^N \nu_{ki} h_i = \Delta_r H_k \quad \frac{d\dot{Q}}{dV_R} = \omega(T_e - T) \frac{dS_t}{dV_R} \quad \text{Circular cross section}$$

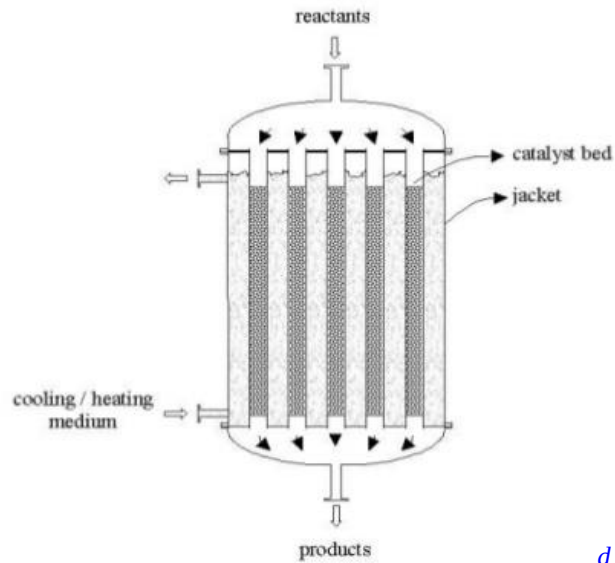
$$\frac{dT}{dV_R} = \frac{1}{\sum_{i=1}^N F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right] \quad \frac{dS_t}{dV_R} = \frac{\pi d_R dz}{\pi \frac{d_R^2}{4} dz}$$

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4 \sum_{i=1}^N F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right]$$

Ex.: Reactor for phthalic anhydride production



Reaction	Kinetics $[r_{V,j}] = \text{mol m}^{-3}\text{s}^{-1}$	Kinetic constants $[k_f] = \text{mol m}^{-3}\text{s}^{-1}\text{bar}^{-2}$ $[T] = \text{K}$
$\text{C}_8\text{H}_{10(g)} + 3\text{O}_{2(g)} \rightarrow \text{C}_8\text{H}_4\text{O}_{3(g)} + 3\text{H}_2\text{O}_{(g)}$	$r_{V,1} = k_1 P_{\text{C}_8\text{H}_{10}} P_{\text{O}_2}$	$\ln k_1 = 25,73 - \frac{13588}{T}$
$\text{C}_8\text{H}_4\text{O}_{3(g)} + 7,5\text{O}_{2(g)} \rightarrow 8\text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$	$r_{V,2} = k_2 P_{\text{C}_8\text{H}_4\text{O}_3} P_{\text{O}_2}$	$\ln k_2 = 26,75 - \frac{15803}{T}$
$\text{C}_8\text{H}_{10(g)} + 10,5\text{O}_{2(g)} \rightarrow 8\text{CO}_{2(g)} + 5\text{H}_2\text{O}_{(g)}$	$r_{V,3} = k_3 P_{\text{C}_8\text{H}_{10}} P_{\text{O}_2}$	$\ln k_3 = 24,86 - \frac{14394}{T}$



$$i = 1(o - xylene) \frac{dF_1}{dx} = A_R \left[(-1)r_{V,1} + (-1)r_{V,3} \right]$$

$$i = 2(oxygene) \frac{dF_2}{dx} = A_R \left[(-3)r_{V,1} + (-7.5)r_{V,2} + (-10.5)r_{V,3} \right]$$

The molar balances of species

$$\frac{dF_i}{dx} = A_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \quad i = 1, 6 \quad \Rightarrow \quad i = 3(water) \frac{dF_3}{dx} = A_R \left[(+3)r_{V,1} + (+2)r_{V,2} + (+5)r_{V,3} \right]$$

$$i = 4(PA) \frac{dF_4}{dx} = A_R \left[(+1)r_{V,1} + (-1)r_{V,2} \right]$$

$$i = 5(CO_2) \frac{dF_5}{dx} = A_R \left[(+8)r_{V,2} + (+8)r_{V,3} \right]$$

$$i = 6(N_2) \frac{dF_6}{dx} = 0$$

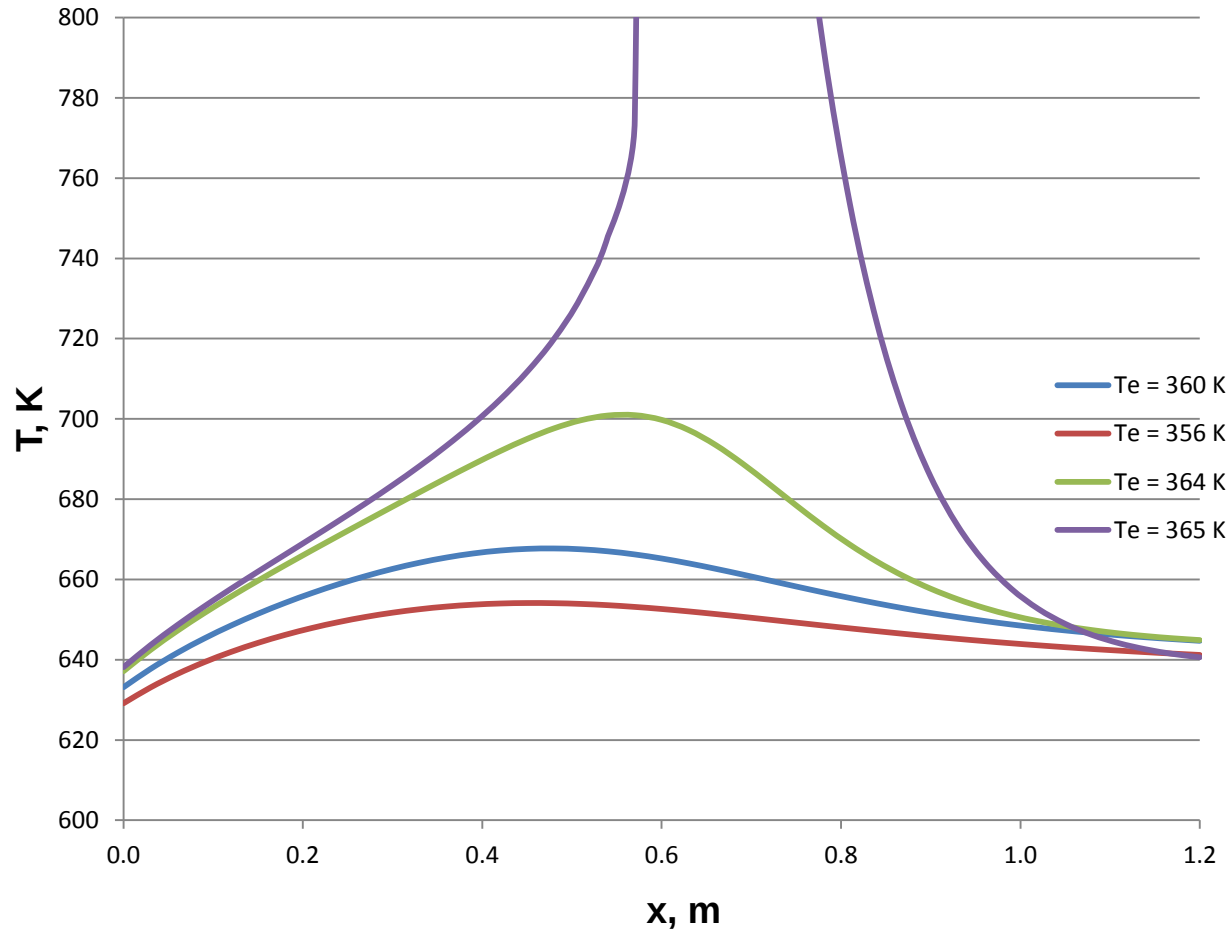
Enthalpy balance

$$\frac{dT}{dx} = \frac{A_R}{F \bar{C}_{pm}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right]$$

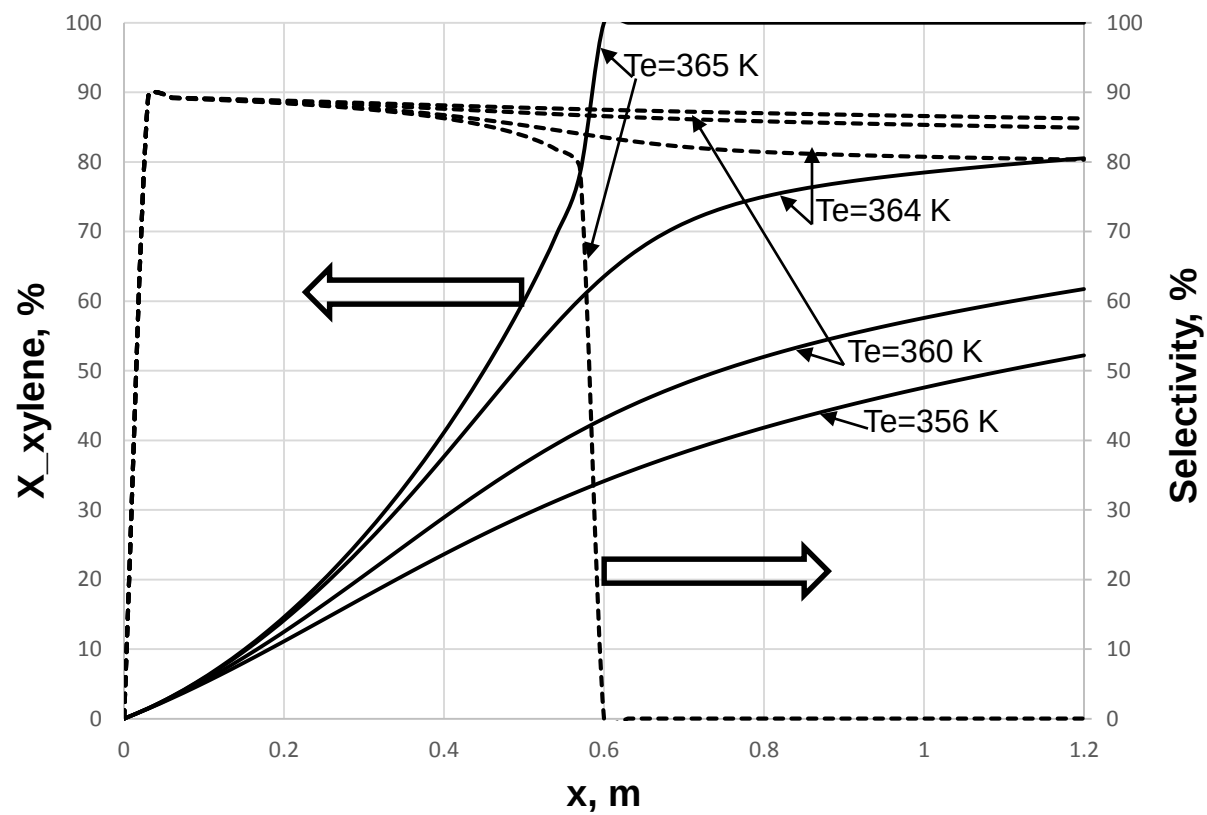
Numerical values of parameters

Mean molar heat capacity, $\text{J mol}^{-1}\text{K}^{-1}$	34.4
Global coefficient of heat transfer , $\text{W m}^{-2}\text{K}^{-1}$	96.116
Pressure, bar	1.0
$\Delta_r H_1$, kJ mol^{-1}	-1116.06
$\Delta_r H_2$, kJ mol^{-1}	-3260.30
$\Delta_r H_3$, kJ mol^{-1}	-4376.36
F_o , mol/s	0.02225
d_R , cm	2.54
Initial composition: 1 % mol C_8H_{10} , 21,1 % O_2 , + N_2	
Reactor tube length, m	1.2

Temperature profiles



Xylene conversion and PA selectivity



One reaction, constant heat capacity of species.
Profiles of conversion and temperature are given by following equations:

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4F^o \left[\sum_{i=1}^N y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|} \Delta c_p X_j \right]} \left[(-\Delta H_r) r_V + \frac{4\omega}{d_R} (T_e - T) \right]$$

$$\frac{dX_j}{dz} = -\frac{\pi \cdot d_R^2}{4} \frac{\nu_j}{F_j^o} r_V(X_j, T) = \frac{\pi \cdot d_R^2}{4} \frac{|\nu_j|}{F_j^o} r_V(X_j, T)$$

$z = 0, T = T_o, X_j = 0$

$$\frac{dF_i}{dV_R} = \nu_i r_V = \frac{\nu_i}{\nu_j} \frac{dF_j}{dV_R}$$

$$X_j = \frac{F_j^o - F_j}{F_j^o}$$

$$F_i - F_i^o = \frac{\nu_i}{\nu_j} (F_j - F_j^o) = -\frac{\nu_i}{\nu_j} F_j^o X_j$$

$$\sum_{i=1}^N F_i c_{p,i} = \sum_{i=1}^N c_{p,i} \left(F_i^o - \frac{\nu_i}{\nu_j} F_j^o X_j \right) =$$

$$= F^o \left[\sum_{i=1}^N y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|} \Delta c_p X_j \right]$$

Limiting cases

1. Isothermal reactor

$$\frac{dT}{dz} = 0 = \left[(-\Delta H_r) r_V + \frac{4\kappa}{d_R} (T_e - T) \right] \Rightarrow (-\Delta H_r) r_V = -\frac{4\omega}{d_R} (T_e - T)$$

$$T = T_o$$

2. Adiabatic reactor

$$\begin{aligned} \frac{dT}{dz} &= \frac{\pi d_R^2}{4F^o \left[\sum_{i=1}^N y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|} \Delta c_p X_j \right]} [(-\Delta H_r) r_V] = \frac{F_j^o (-\Delta H_r)}{|\nu_j| F^o \left[\sum_{i=1}^N y_i^o c_{p,i} + \frac{y_j^o}{|\nu_j|} \Delta c_p X_j \right]} \frac{dX_j}{dz} = \\ &= \frac{y_j^o (-\Delta_r H^o - \Delta c_p (T - T^o))}{\left[|\nu_j| \sum_{i=1}^N y_i^o c_{p,i} + y_j^o \Delta c_p X_j \right]} \frac{dX_j}{dz} \\ \int_{T^o}^T \frac{dT}{y_j^o (-\Delta_r H^o - \Delta c_p (T - T^o))} &= \int_0^{X_j} \frac{dX_j}{\left[|\nu_j| \sum_{i=1}^N y_i^o c_{p,i} + y_j^o \Delta c_p X_j \right]} \end{aligned}$$

$$T = T^o + \frac{y_j^o (-\Delta_r H^o) X_j}{|\nu_j| \sum_{i=1}^N y_i^o c_{p,i} + y_j^o \Delta c_p X_j}$$

Cf. adiabatic BATCH and CSTR

One reaction, constant heat capacity of reaction mixture.
 Profiles of conversion and temperature are given by following equations:

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4 F^o \bar{c}_{pM}} \left[(-\Delta H_r) r_V + \frac{4\omega}{d_R} (T_e - T) \right]$$

$$\frac{dX_j}{dz} = - \frac{\pi d_R^2}{4} \frac{\nu_j}{F_j^o} r_V(X_j, T) = \frac{\pi d_R^2}{4} \frac{|\nu_j|}{F_j^o} r_V(X_j, T)$$

$z = 0, T = T_o, X_j = 0$

$$\sum_{i=1}^N F_i c_{p,i} = \sum_{i=1}^N F y_i c_{p,i} \cong$$

$$\cong F^o \sum_{i=1}^N y_i^o c_{p,i} = F^o \bar{c}_{pM}^o$$

Limiting cases

1. Isothermal reactor

$$\frac{dT}{dz} = 0 = \left[(-\Delta H_r) r_V + \frac{4\kappa}{d_R} (T_e - T) \right] \Rightarrow (-\Delta H_r) r_V = - \frac{4\omega}{d_R} (T_e - T)$$

$T = T_o$

2. Adiabatic reactor

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4 F^o \bar{c}_{pM}} [(-\Delta H_r) r_V] = \frac{F_j^o (-\Delta H_r)}{|\nu_j| F^o \bar{c}_{pM}} \frac{dX_j}{dz}$$

$$T = T_o + \frac{y_j^o (-\Delta H_r)}{|\nu_j| \bar{c}_{pM}^o} X_j$$

Exercise: reactor for oxidation of SO_2 to SO_3

Numerical method:

- Euler method

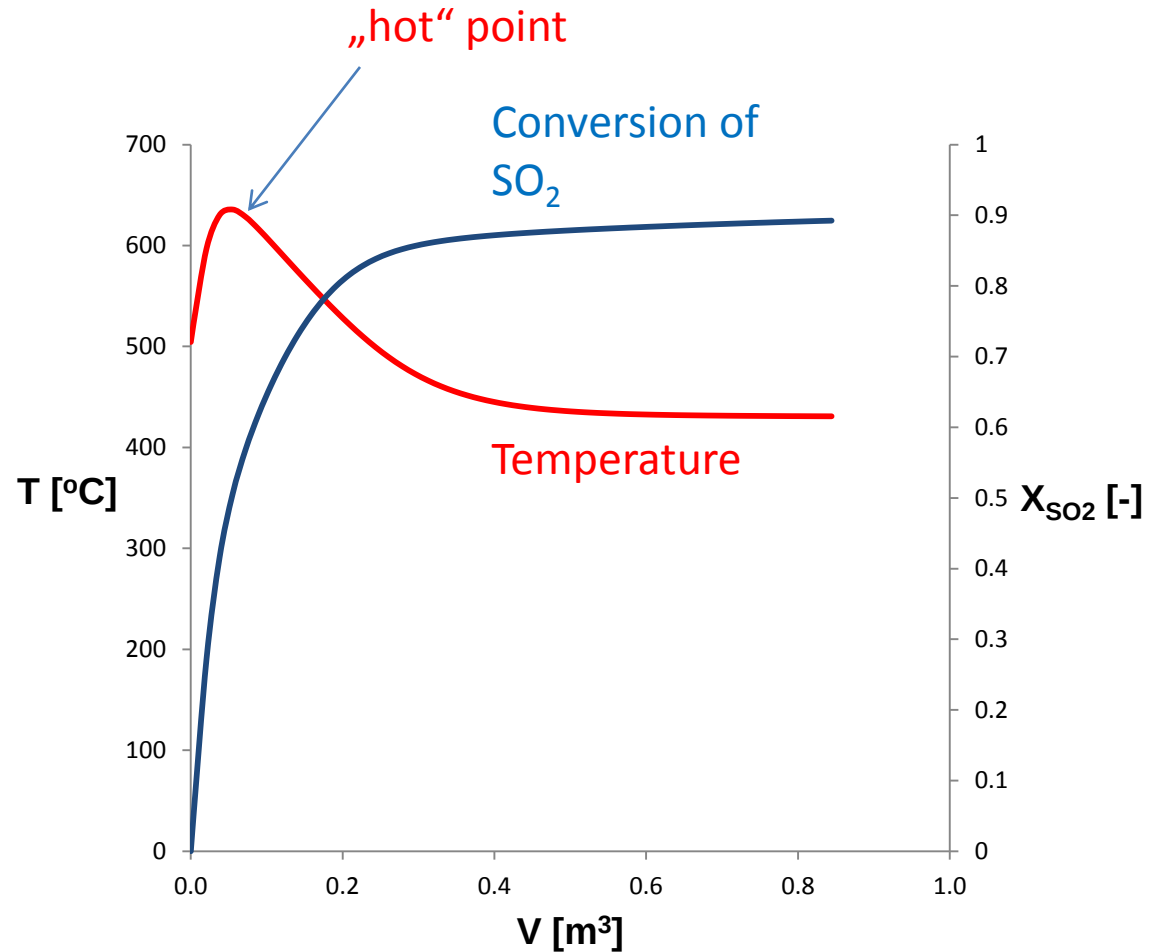
„Stiff“ solvers

MATLAB

www.netlib.org

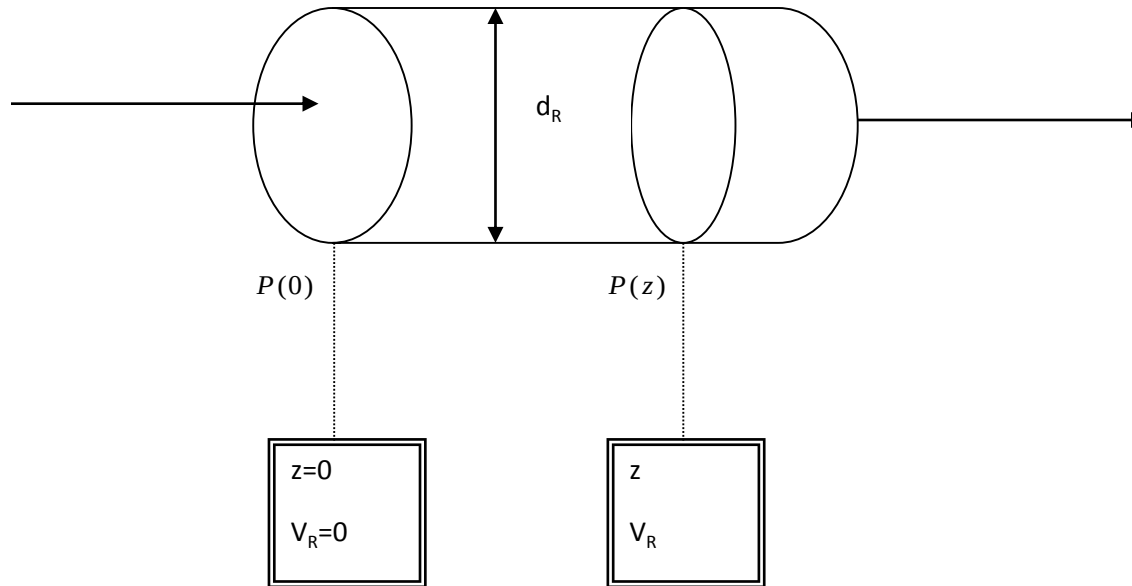
www.athenavisual.com

http://wxmaxima.sourceforge.net/wiki/index.php/Main_Page



Balance of mechanical energy in PFR

Profile of overall pressure (P(z))



Pressure drop and friction coefficient (factor) in laminar and turbulent flow

$$\frac{P(0) - P(z)}{\rho_f} = \lambda \frac{z}{d_R} v^2$$

$$-\frac{dP}{dz} = \lambda \frac{\rho_f}{d_R} v^2$$

ρ_f density of fluid(kg/m³)

λ friction coefficient(-)

$$\lambda = f(\text{Re}, \varepsilon_w / d_R) \longrightarrow$$

v fluid mean velocity

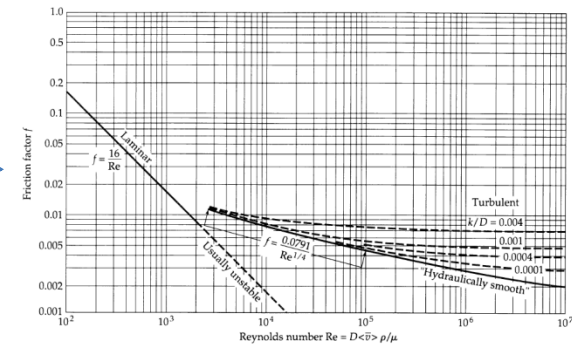


Fig. 6.2-2. Friction factor for tube flow (see definition of f in Eqs. 6.1-2 and 6.1-3. [Curves of L. F. Moody, *Trans. ASME*, 66, 671-684 (1944) as presented in W. L. McCabe and J. C. Smith, *Unit Operations of Chemical Engineering*, McGraw-Hill, New York (1954).]

Catalytic PFR

Profile of pressure is calculated using Ergun equation:

$$-\frac{dP}{dz} = 150 \frac{\mu_f}{d_p^2} \frac{(1 - \varepsilon_b)^2}{\varepsilon_b^3} v_f^o + 1.75 \frac{\rho_f}{d_p} \frac{1 - \varepsilon_b}{\varepsilon_b^3} (v_f^o)^2 = A_1 \mu_f v_f^o + A_2 \rho_f (v_f^o)^2$$

μ_f - fluid dynamic viscosity (Pa.s)

ρ_f - fluid density (kg/m³)

v_f^o - superficial fluid mean velocity (m/s)

ε_b - bed porosity (-)

d_p - catalyst particle diameter (m)

PFR model for one reaction with constant heat capacity of reaction mixture

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4 F^o \bar{c}_{pM}} \left[(-\Delta H_r) r_V + \frac{4\omega}{d_R} (T_e - T) \right]$$

$$\frac{dX_j}{dz} = - \frac{\pi \cdot d_R^2}{4} \frac{v_j}{F_j^o} r_V(X_j, T) = \frac{\pi \cdot d_R^2}{4} \frac{|v_j|}{F_j^o} r_V(X_j, T)$$

$$\frac{dP}{dz} = - \left[A_1 \mu_f v_f^o + A_2 \rho_f (v_f^o)^2 \right]$$

$$z = 0, \quad T = T_o, \quad X_j = 0, \quad P = P_o$$

Summary

Energy = Internal Energy + Kinetic + Potential + ... $\cong$ Internal Energy $\Rightarrow$ Enthalpy $H(T, P, n_1, n_2, \dots, n_N)$

Ideal mixture : $H(T, P, n_1, n_2, \dots, n_N) = \sum_{i=1}^N n_i h_i(T) \quad h_i(T) = h_i(T_o) + \int_{T_o}^T c_{p,i}(T) dT$

BATCH : $\frac{dH}{dt} = \dot{Q}$

$$\frac{dH}{dt} = \frac{d \sum_{i=1}^N n_i h_i}{dt} = \sum_{i=1}^N \left[\frac{dn_i}{dt} h_i + n_i \frac{dh_i}{dT} \frac{dT}{dt} \right] = \sum_{i=1}^N \left[\sum_{k=1}^{NR} \nu_{ki} r_{V,k} V_R h_i + n_i c_{p,i} \frac{dT}{dt} \right] =$$

$$= \left[\sum_{k=1}^{NR} \Delta_r H_k r_{V,k} V_R + \sum_{i=1}^N n_i c_{p,i} \frac{dT}{dt} \right] = \dot{Q}$$

$$\sum_{i=1}^N n_i c_{p,i} \frac{dT}{dt} = \rho_m c_P V_R \frac{dT}{dt} = \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} V_R + \dot{Q} \right] = \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} V_R + S_H \omega (T_e - T) \right]$$

$$\rho_m c_P V_R \frac{dT}{dt} = V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + S_H \omega (T_e - T) \quad \frac{dn_i}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} V_R$$

$V_R = f(t)$state behavior, initial conditions: $t = 0, T = T_o, n_i = n_i^o$

Ideal mixture, steady state CSTR:

$$\sum_{i=1}^N F_i^o h_i^o - \sum_{i=1}^N F_i h_i + \dot{Q} = 0$$

$$F_i^o - F_i + V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k} = 0, \quad i = 1, N$$

$$\Delta_r H_k = \sum_{i=1}^N \nu_{ki} h_i$$

$$V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \sum_{i=1}^N F_i^o (h_i^o - h_i) + \dot{Q} = 0$$

$$\text{constant } c_{p,i} : V_R \sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \sum_{i=1}^N F_i^o c_{p,i} (T_o - T) + \dot{Q} = 0$$

$$V_R \sum_{k=1}^{NR} \left(-\Delta_r H_k(T_o) - \Delta c_{p,k} (T - T^o) \right) r_{V,k} + F^o (T - T^o) \sum_{i=1}^N y_i^o c_{pi} + \dot{Q} = 0$$

Ideal mixture, steady state PFR: $\frac{d}{dV_R} \left(\sum_{i=1}^N F_i \bar{H}_i \right) = \frac{d}{dV_R} \left(\sum_{i=1}^N F_i h_i \right) = \frac{d\dot{Q}}{dV_R}$

$$\sum_{i=1}^N \left(\frac{dF_i}{dV_R} h_i(T) + F_i \frac{dh_i(T)}{dV_R} \right) = \sum_{i=1}^N \left(\sum_{k=1}^{NR} \nu_{ki} r_{V,k} h_i(T) + F_i \frac{dh_i(T)}{dT} \frac{dT}{dV_R} \right) =$$

$$= \sum_{k=1}^{NR} \Delta_r H_k r_{V,k} + \frac{dT}{dV_R} \sum_{i=1}^N F_i c_{pi} = \frac{d\dot{Q}}{dV_R} \quad \Delta_r H_k = \sum_{i=1}^N \nu_{ki} h_i$$

$$\frac{dF_i}{dV_R} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \quad \sum_{i=1}^N \nu_{ki} h_i = \Delta_r H_k \quad \frac{d\dot{Q}}{dV_R} = \omega(T_e - T) \frac{dS_t}{dV_R}$$

$$\frac{dT}{dV_R} = \frac{1}{\sum_{i=1}^N F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right] \quad \text{Cylinder} \quad \frac{dS_t}{dV_R} = \frac{\pi d_R dz}{\pi \frac{d_R^2}{4} dz} = \frac{4}{d_R}$$

$$\frac{dT}{dz} = \frac{\pi d_R^2}{4 \sum_{i=1}^N F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right]$$

Example

A gas phase reaction between butadiene and ethylene is conducted in a PFR, producing cyclohexene:



The feed contains equimolar amounts of each reactant at 525 °C and the total pressure of 101 kPa. The enthalpy of reaction at inlet temperature is -115 kJ/mol and reaction is second-order:

$$r_V = k(T)c_1c_2 \\ k(T) = 3.2 \times 10^4 \exp \left[-\frac{115148.9}{RT} \right] \quad (\text{mol}^{-1}\text{m}^{-3}\text{s}^{-1})$$

Assuming the process is adiabatic and isobaric, determine the volume of reactor and the residence time for 25 % conversion of butadiene.

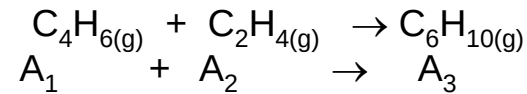
Data:

Mean heat capacities of components are as follows (supposing that heat capacities are constant in given range of temperature)

$$c_{p1} = 150 \text{ J.mol}^{-1}.\text{K}^{-1}, c_{p2} = 80 \text{ J.mol}^{-1}.\text{K}^{-1}, c_{p3} = 250 \text{ J.mol}^{-1}.\text{K}^{-1}$$

Project 15

A gas phase reaction between butadiene and ethylene is conducted in a PFR, producing cyclohexene:



The feed contains equimolar amounts of each reactant at 525 °C and the total pressure of 101 kPa. The enthalpy of reaction at inlet temperature is -115 kJ/mol and reaction is second-order:

$$r_v = k(T)c_1c_2$$

$$k(T) = 3.2 \times 10^4 \exp \left[-\frac{115148.9}{RT} \right] \quad (\text{mol}^{-1}\text{m}^{-3}\text{s}^{-1})$$

1. Calculate temperature and conversion profiles in adiabatic PFR.
2. Assuming the process is adiabatic and isobaric, determine the volume of reactor and the residence time for 25 % conversion of butadiene.

Data:

Heat capacities of components will be taken from open resources [1,2]

1. <http://webbook.nist.gov/chemistry/>
2. B. E. Poling, J.M.Prausnitz, J.P.O'Connell, The Properties of Gases and Liquids, Fifth Edition, McGraw-Hill, N.Y. 2001.

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