6. Energy balance on chemical reactors

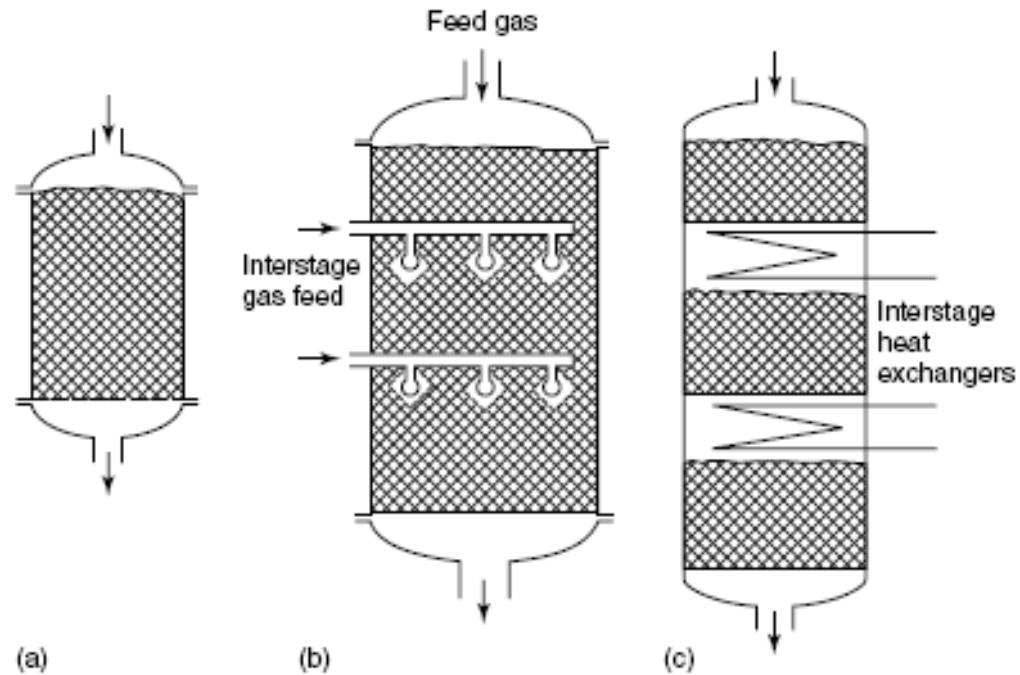Most of reactions are not carried out isothermally

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.
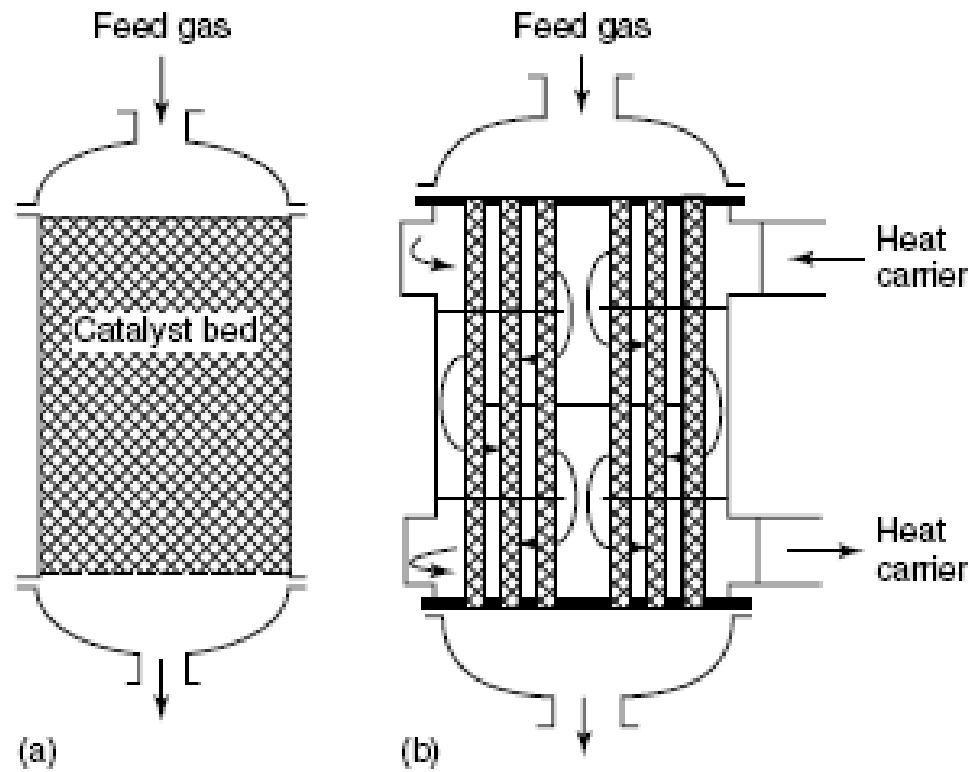
Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.
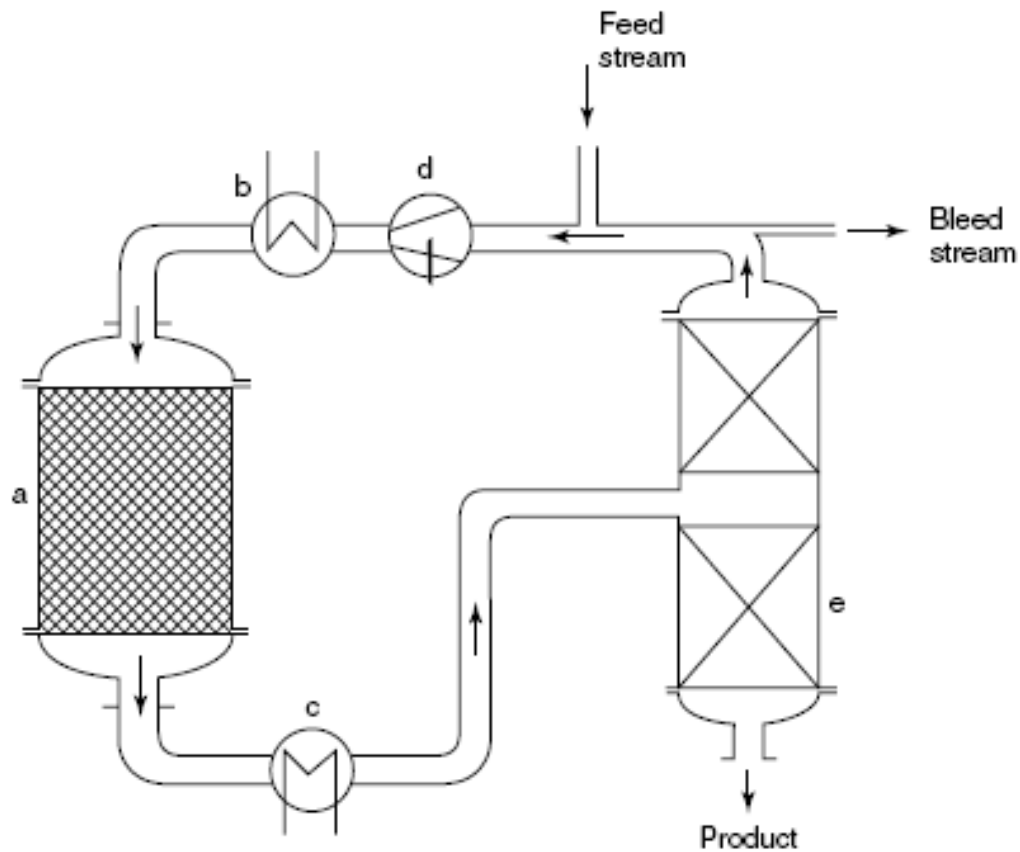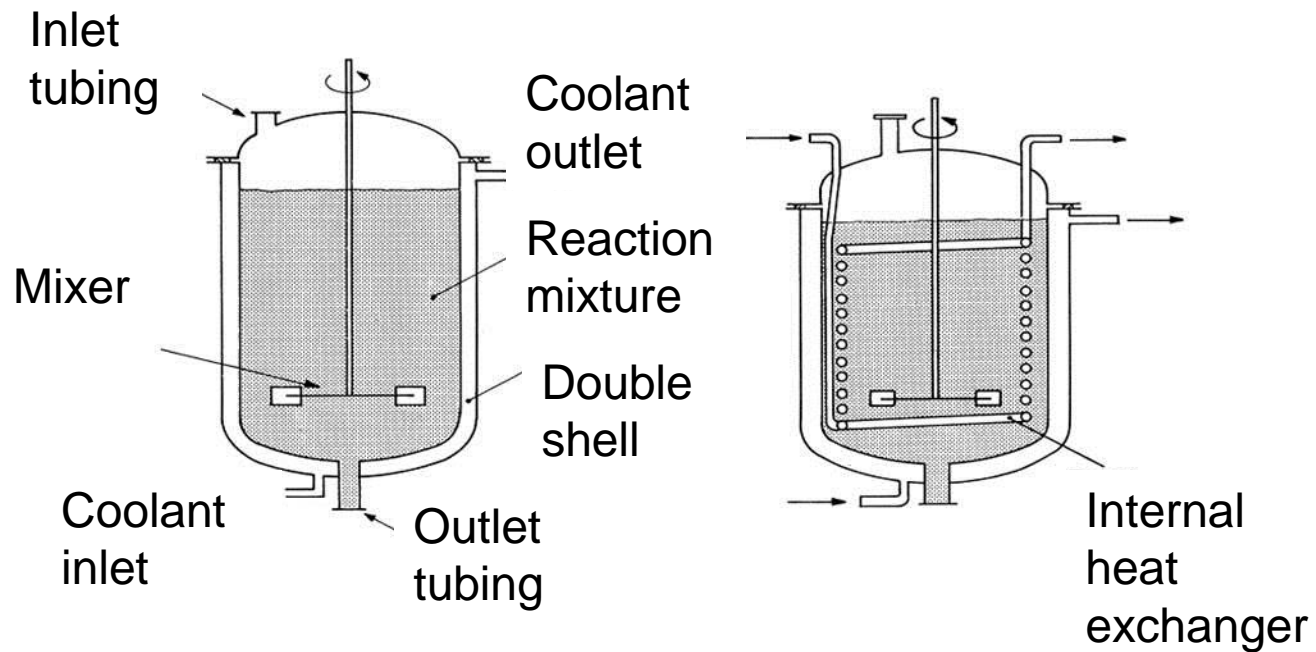
Fig. 2 Reaction cycle for synthesis reactions with incomplete conversion. (a) Fixed-bed reactor; (b) feed preheater; (c) exit cooler; (d) recirculation compressor; (e) separation device.

BATCH or CSTR heated (cooled) reactors

Inlet tubing

Coolant outlet

Reaction mixture

Mixer

Double shell

Coolant inlet

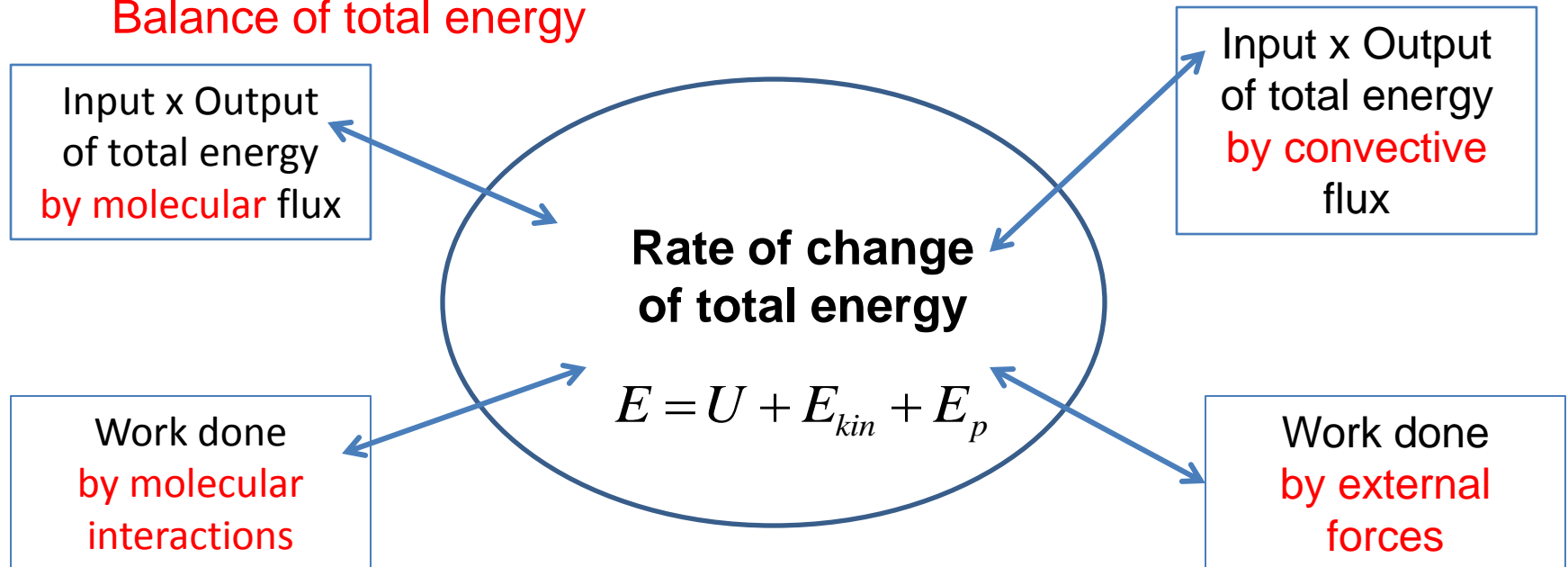Outlet tubing

Internal heat exchanger

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

Input x Output
of total energy
by molecular flux

Input x Output
of total energy
by convective
flux

Rate of change
of total energy

$$E = U + E_{kin} + E_p$$

Work done
by molecular
interactions

Work done
by external
forces

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

Rate of work done on surroundings [W]

Heat flux [W]

$$\dot{W}$$

$$\dot{Q}$$

$$F_1$$
$$T_1$$
$$y_i^1$$
$$P_1$$
$$e_1$$

$$F_o$$
$$T_o$$
$$y_i^o$$
$$P_o$$
$$e_o$$

$$E = \int_{V_R} e_V \, dV$$

$$E, \ V_R$$

Single phase reacting system
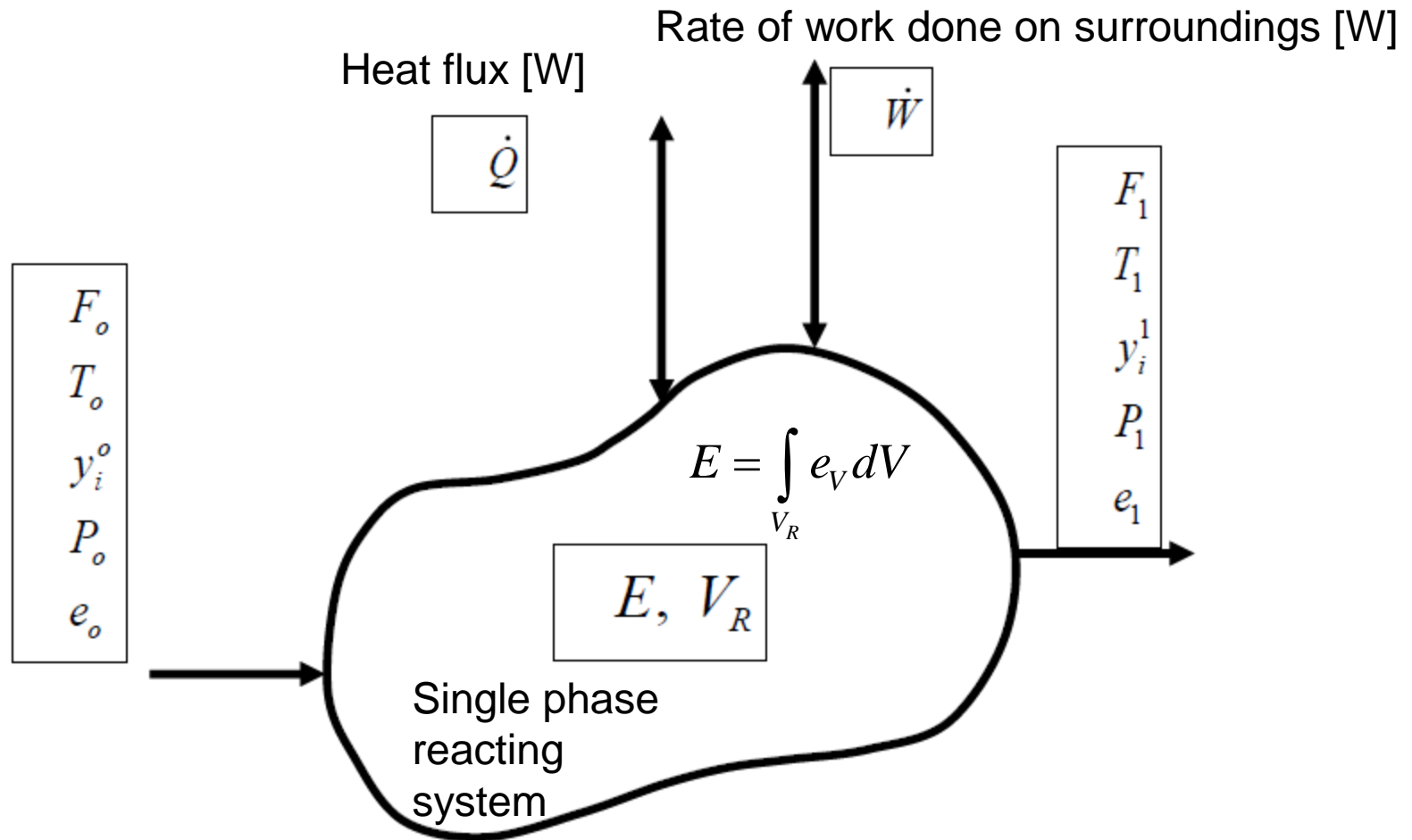
e_o, e_1 – specific total energy of inlet (outlet) streams [J/mol]
V_R – volume of reaction mixture [m³]

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

$e_o, e_1 -$ 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 $-P\dfrac{dV_R}{dt}$

- Work done by electric, magnetic fields $\dot{W}_f$

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

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

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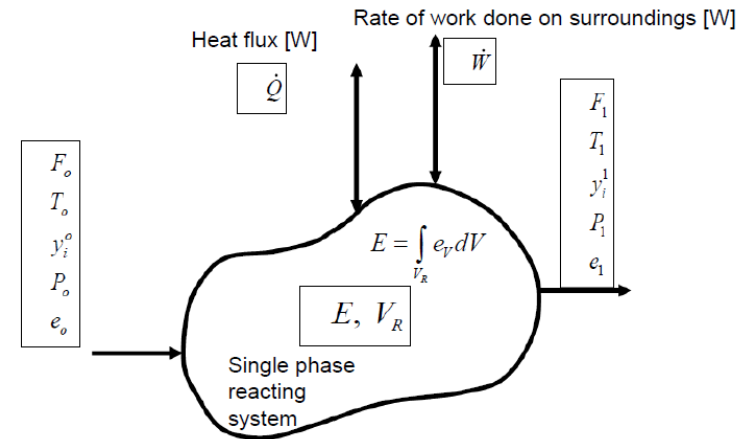
From enthalpy definition

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

Introducing partial molar enthalpies of species

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

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

Rate of work done on surroundings [W]

Heat flux [W]

$\dot{Q}$

$\dot{W}$

F_o
T_o
y_i^o
P_o
e_o

$E = \int_{V_R} e_V dV$

E, V_R

F_1
T_1
y_i^1
P_1
e_1

Single phase reacting system

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/m^3]   Molar heat capacity [J/mol/K]

We know that (from thermodynamics)

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

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

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

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

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

Using definition of the enthalpy of k-th reaction

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

we have

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

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

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

$$V_R = f(t) \quad \longrightarrow \quad \textbf{we need state equation !}$$

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

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

the coefficient of isothermal compressibility

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

the volume variation due to k-th chemical reaction

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

the specific heat capacity at **constant volume**

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

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

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

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

liquid (condensed) systems

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

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

$\omega \;-\;$ the overall (global) heat transfer coefficient $[\mathrm{W.m^{-2}.K^{-1}}]$

$S_H \;-\;$ the heat exchange area $[\mathrm{m^2}]$

$T_e \;-\;$ temperature of external cooling (heating) fluid

Limiting cases

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

Example
Adiabatic reactor with 1 reaction, constant heat capacities

Energy balance on adiabatic BATCH reactor

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

Molar balance of key component

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

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

$$\rho_m V_R c_p = n \sum_{i=1}^{N} y_i c_{pi} = \sum_{i=1}^{N} n_i c_{pi} = \sum_{i=1}^{N} \left(n_i^o - \frac{v_i}{v_j} n_j^o X_j \right) c_{pi} =$$
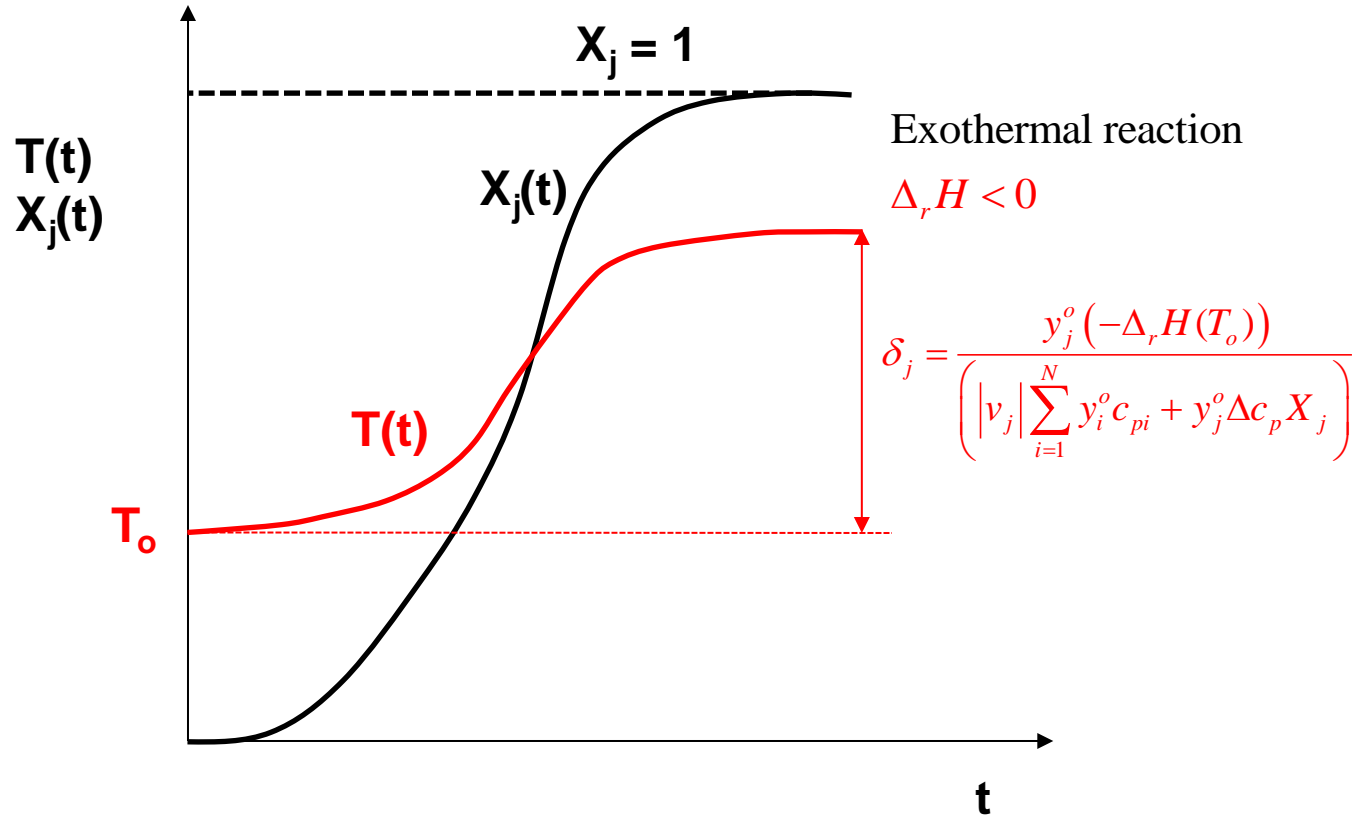
$$= \sum_{i=1}^{N} \left(n_i^o c_{pi} \right) - \frac{n_j^o X_j}{v_j} \sum_{i=1}^{N} \left(v_i c_{pi} \right) = \sum_{i=1}^{N} \left(n_i^o c_{pi} \right) + \frac{n_j^o X_j}{|v_j|} \Delta c_p$$

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

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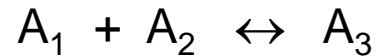
$$\delta_j = \frac{y_j^o \left(-\Delta_r H(T_o)\right)}{\left(|v_j| \sum_{i=1}^{N} y_i^o c_{pi} + y_j^o \Delta c_p X_j \right)} \qquad \text{the adiabatice rise of temperature}$$

Trajectories of T(t) and X_j(t)

$X_j = 1$

T(t)
X_j(t)

X_j(t)

Exothermal reaction

$\Delta_r H < 0$

T(t)

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

T_o

t

Homework 10

The reversible reaction

$$A_1 + A_2 \leftrightarrow A_3$$

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

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

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

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

Initial conditions and thermodynamic data

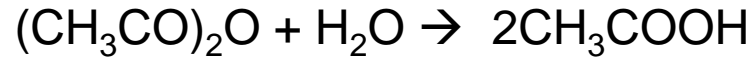$$c_1^o = 0.1 \text{ mol/dm}^3 \qquad\qquad c_{p1} = 25 \text{ J/mol/K}$$

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

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

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

Example

Acetic anhydride reacts with water

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

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

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

Data

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

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

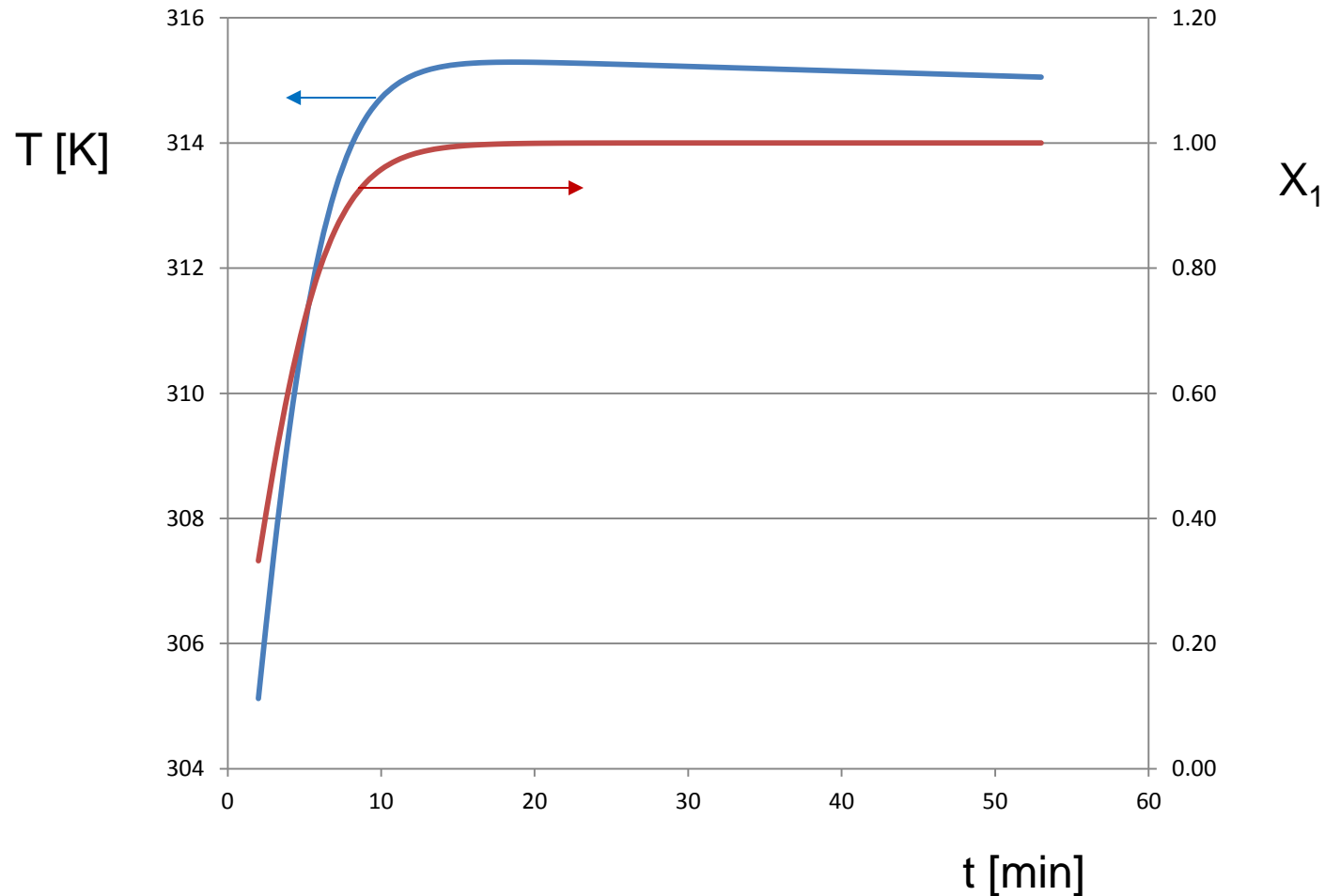w_i^o − initial mass fractions, c_{pMi} - mass heat capacities $(kJ.kg^{-1}.K^{-1}), M_i$ - molar weight $(kg.mol^{-1})$

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

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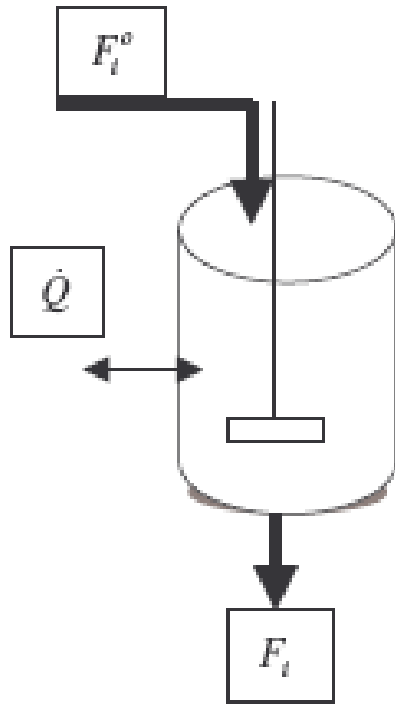
By numerical integration we get

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

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

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

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

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

Molar balance on CSTR

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

We get

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

Enthalpy change for k-th reaction

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

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

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

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

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

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

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

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

Steady state

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

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

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

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

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

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

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

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

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

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

$$G_i\left(T, F_1, F_2, ...F_N\right) = 0, \qquad i = 1, N+1$$

Issues:
• multiple solutions
• slow convergence (divergence)

Example
Adiabatic CSTR with 1 reaction, constant heat capacities

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

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

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

2 nonlinear algebraic equations for unknown *T* and *X_j*

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

$$= T^o + \delta_j X_j \qquad \textbf{cf. adiabatic const.-volume BATCH}$$

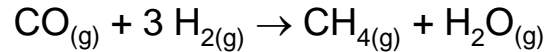# Multiple steady states of adiabatic CSTR (exothermal reaction)

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

f₁(T)

Steady state 1

f₂(T)

Steady state 2

Steady state 3
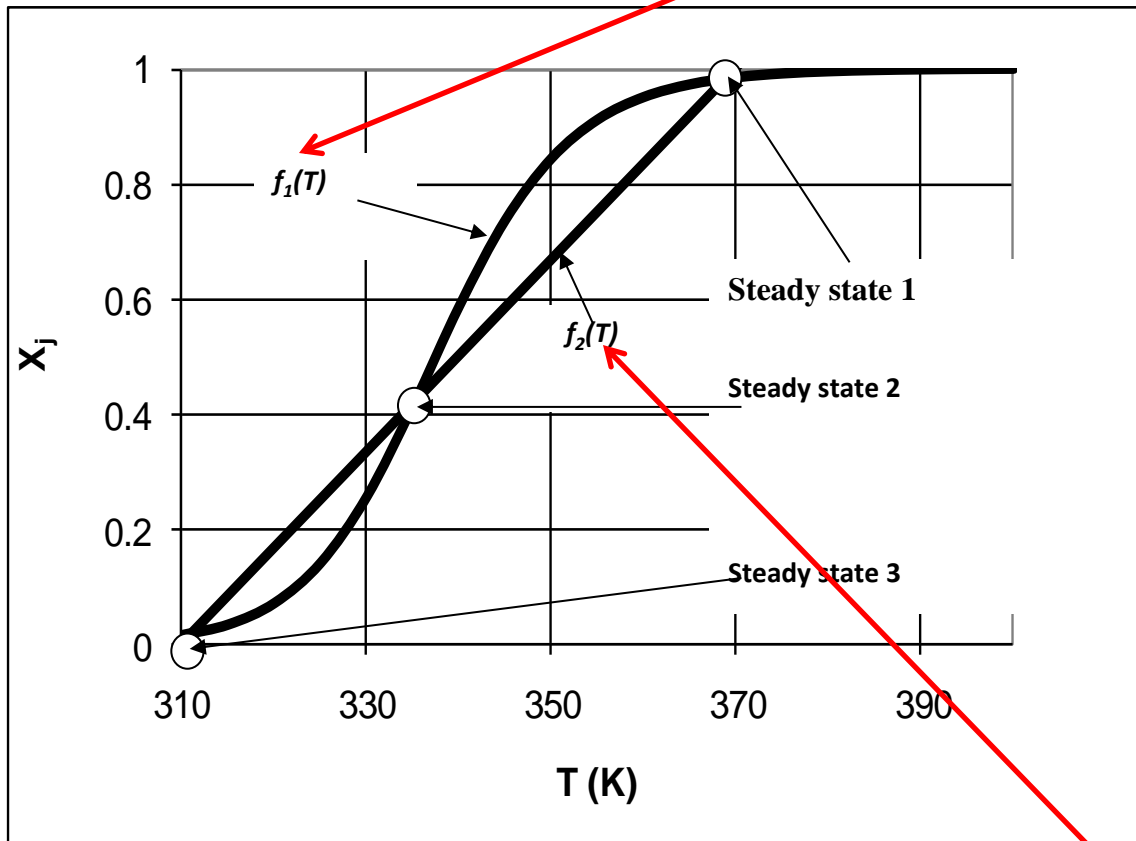
$$T = T_o + \delta_j X_j \Rightarrow X_j = f_2(T)$$

Example

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

$$CO_{(g)} + 3\,H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$$

$$r_V = kc_{CO}$$

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

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

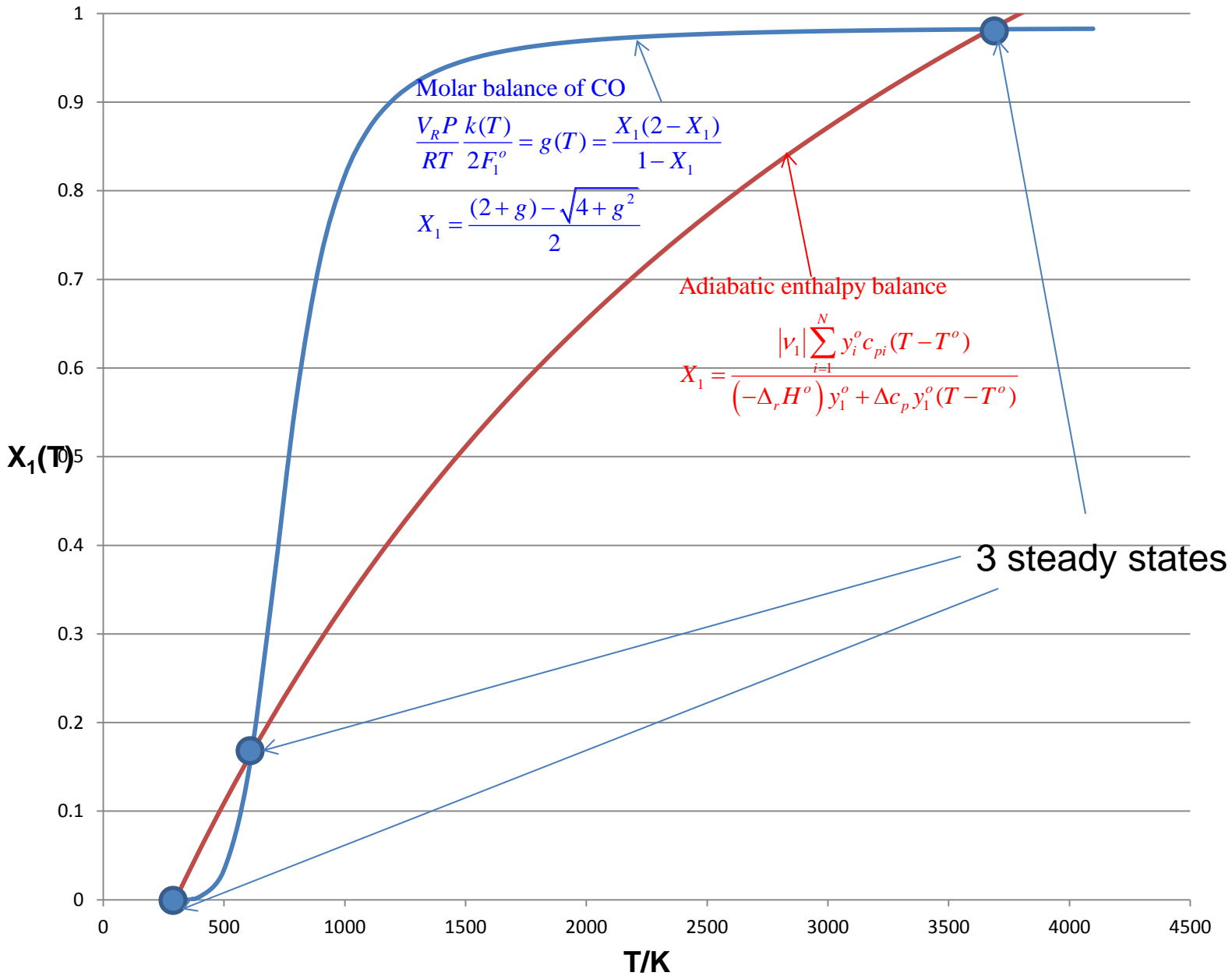The feed to the CSTR consists of CO and H_2 at the following (stoichiometric) concentrations:

$C_{CO}(in) = 0.0102$ mol/liter $C_{H2}(in) = 0.0306$ mol/liter

The heat of reaction at 298 K is equal to –49.0 kcal/mol.
The heat capacities of CO, H_2, CH_4 and H_2O 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.

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

Molar balance of CO

$$\frac{V_R P}{RT} \frac{k(T)}{2F_1^o} = g(T) = \frac{X_1(2 - X_1)}{1 - X_1}$$

$$X_1 = \frac{(2 + g) - \sqrt{4 + g^2}}{2}$$

Adiabatic enthalpy balance

$$X_1 = \frac{|v_1| \sum_{i=1}^{N} y_i^o c_{pi}(T - T^o)}{(-\Delta_r H^o) y_1^o + \Delta c_p y_1^o (T - T^o)}$$

3 steady states

$X_1(T)$

T/K

Remarks:

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

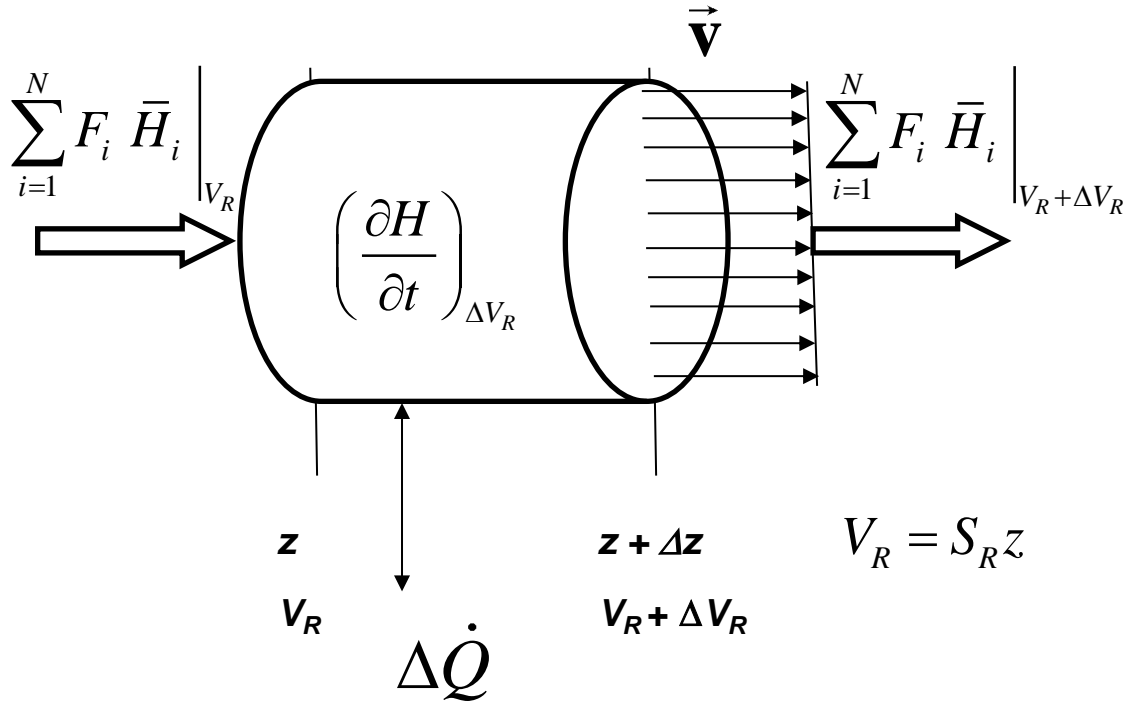Determine steady states of adiabatic CSTR in which the exothermal liquid state reaction takes place

$$A1 \rightarrow A2$$

Reaction rate:

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

Data

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

Balance of enthalpy on Plug Flow Reactor (PFR)

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

in the steady state

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

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

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

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

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

Circular cross section

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\frac{dF_i}{dV_R} = v_i r_V = \frac{v_i}{v_j} \frac{dF_j}{dV_R}$$

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

$$F_i - F_i^o = \frac{v_i}{v_j} \left(F_j - F_j^o \right) = -\frac{v_i}{v_j} F_j^o X_j$$

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

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

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

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

$$= \frac{y_j^o\left(-\Delta_r H^o - \Delta c_p(T-T^o)\right)}{\left[|v_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o \Delta c_p X_j\right]}\frac{dX_j}{dz}$$

$$\int_{T^o}^{T} \frac{dT}{y_j^o\left(-\Delta_r H^o - \Delta c_p(T-T^o)\right)} = \int_{0}^{X_j} \frac{dX_j}{\left[|v_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o \Delta c_p X_j\right]}$$

$$T = T^o + \frac{y_j^o(-\Delta_r H^o)X_j}{|v_j|\sum_{i=1}^{N} y_i^o c_{p,i} + y_j^o \Delta c_p X_j}$$ **Cf. adiabatic BATCH and CSTR**

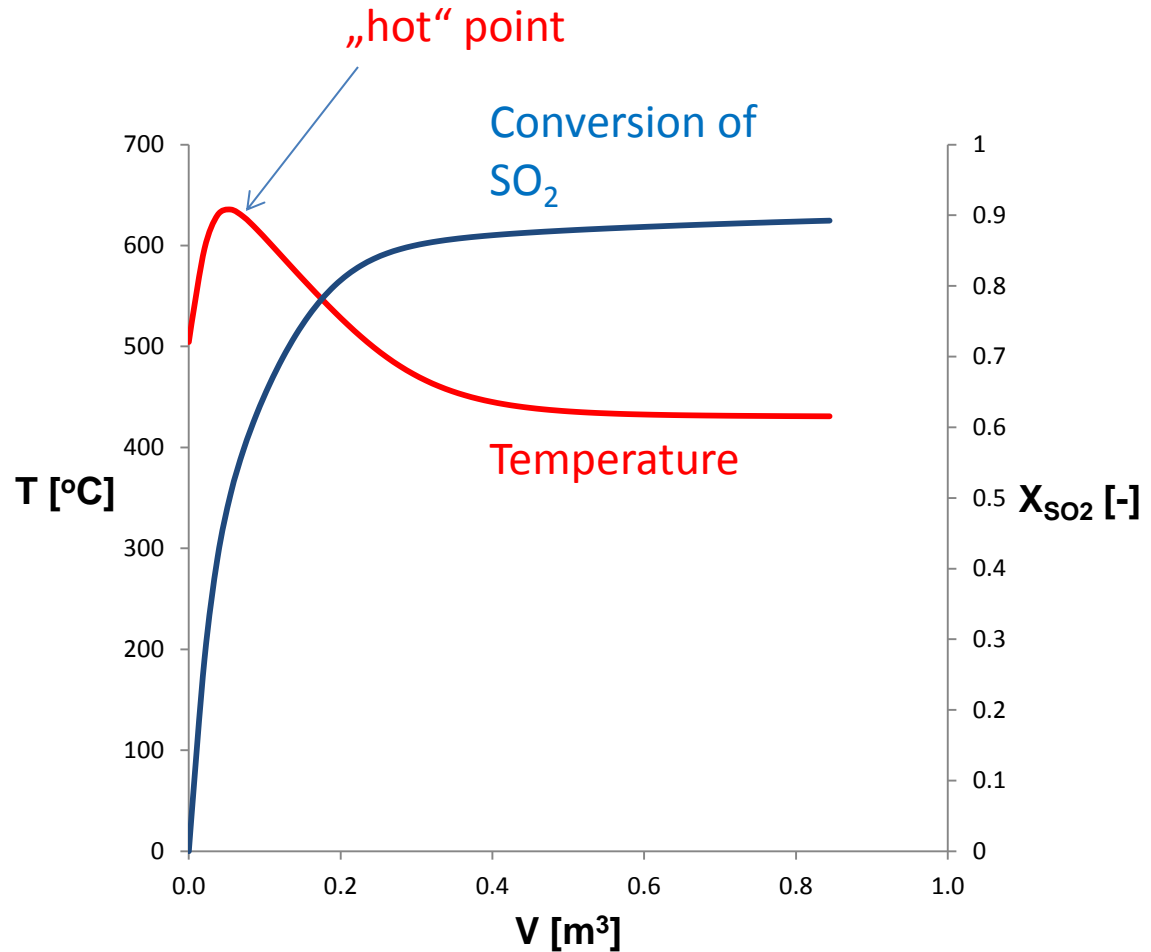# Exercise: reactor for oxidation of SO_2 to SO_3

Numerical method:
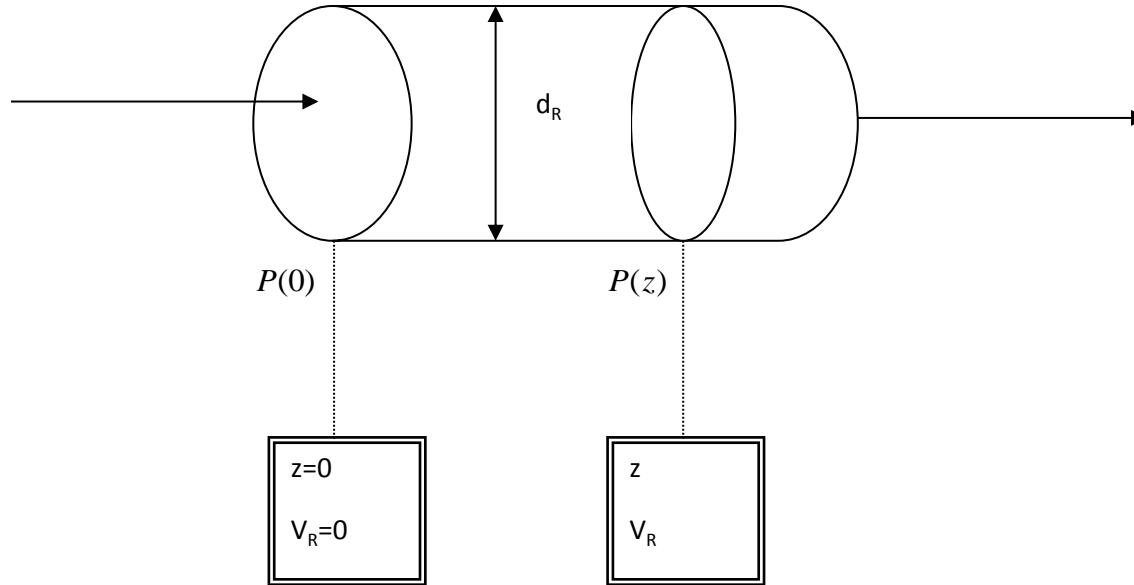• **Euler method**

"Stiff" solvers MATLAB
www.netlib.org
www.athenavisual.com
http://wxmaxima.sourceforge.net/wiki/index.php/Main_Page

"hot" point

Conversion of SO_2

Temperature

T [°C]

X_{SO2} [-]

V [m³]

Balance of mechanical energy in PFR
Profile of overall pressure (P(z))

$P(0)$ $P(z)$

z=0	z
$V_R=0$	V_R

Bernoulli equation

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

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

ρ_f **density of fluid(kg/m3)**

λ **friction coefficient(-)**

$$\lambda = f(\mathrm{Re}, \varepsilon_w / d_R)$$
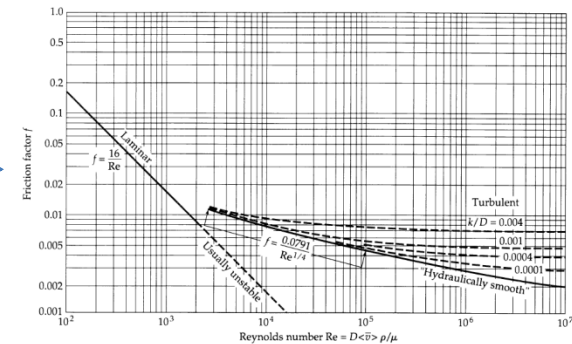
v **fluid mean velocity**

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:

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

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

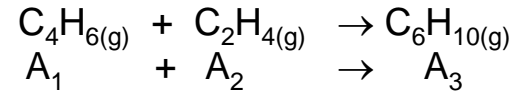$$\frac{dT}{dz} = \frac{\pi d_R^2}{4F^o \overline{c}_{pM}^o} \left[(-\Delta H_r) r_V + \frac{4\omega}{d_R} (T_e - T) \right]$$

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

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

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

Example

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

$$C_4H_{6(g)} + C_2H_{4(g)} \rightarrow C_6H_{10(g)}$$
$$A_1 \quad + \quad A_2 \quad \rightarrow \quad A_3$$

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:

$$r_V = k(T)c_1 c_2$$

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

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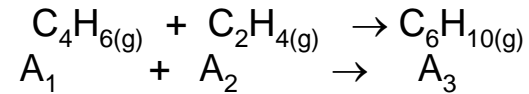
Data:

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

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

Project 15

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

$$C_4H_{6(g)} + C_2H_{4(g)} \rightarrow C_6H_{10(g)}$$
$$A_1 + A_2 \rightarrow A_3$$

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:

$$r_V = k(T)c_1c_2$$

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

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.