

APPLIED REACTION KINETICS

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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

Resources and references

- **Notes from lectures**

- **Internet**

web.vscht.cz/bernaudem/

- **Textbooks**

Fogler Scott H.: Elements of Chemical Reaction Engineering, 4th Edition, Prentice Hall, 2006. (<http://www.engin.umich.edu/~cre/>)

Missen R.W., Mims C.A., Saville B.A., Introduction to Chemical Reaction Engineering and Kinetics, J. Wiley&Sons, N.Y. 1999.

- **Journals (on-line)**

- **Software**

MS Excel, (**Matlab**, Octave, Athena Visual Studio, FORTRAN, Maple....)

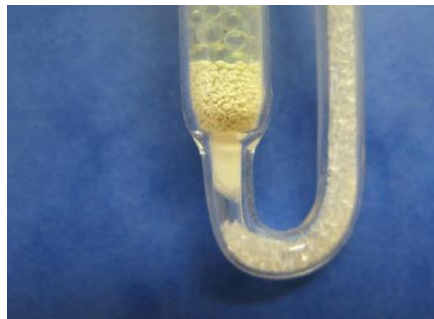


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Fischer-Tropsch (SASOL, RSA)



N₂O decomposition (IPC AS, CZ)



WGS (BASF, FRG)



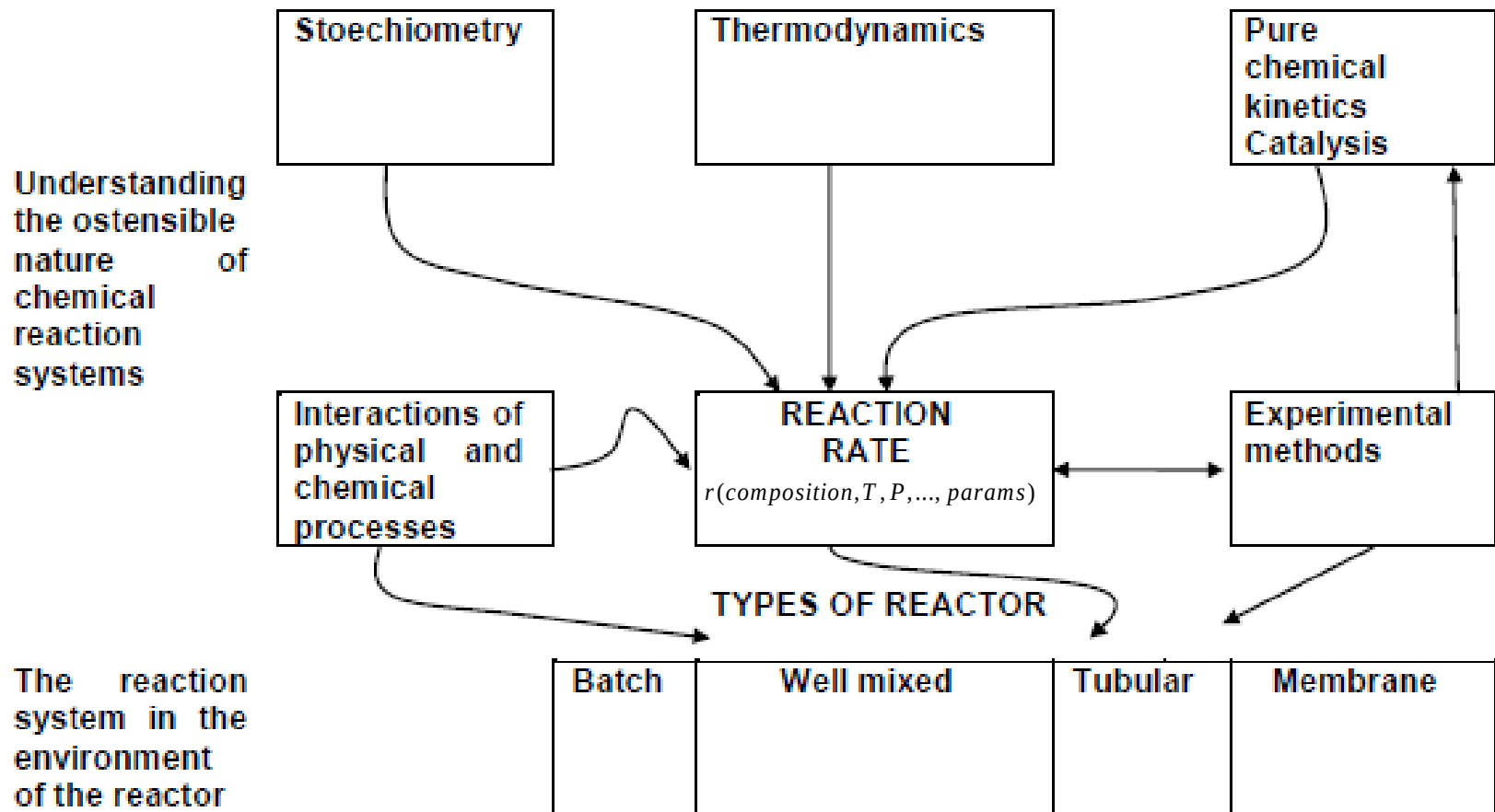
Chemical **reactor**(s) → **heart** of chemical process



Methane aromatization (ICTP, CZ)



Raw material → separation → **reaction** → separation → product



Material and energy balances
 Stability, transient behavior
 Imperfections of models
 Industrial chemical reactors, design, optimization, software

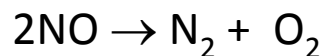
Summary of the 1st lecture

- Stoichiometry
- Extent of reaction
- Fractional conversion of key component
- Stoichiometric matrix
- Balance of chemical elements
- Selectivity, Yield
- Reaction rate definition

Stoichiometry

"στοιχείον" the material element (Plato)

"μέτρον" the count, the quantity



closed (batch) system

	t = 0	t > 0
Atoms of oxygen	$n_{\text{NO}}^o + 2n_{\text{O}_2}^o =$	$n_{\text{NO}} + 2n_{\text{O}_2}$
Atoms of nitrogen	$n_{\text{NO}}^o + 2n_{\text{N}_2}^o =$	$n_{\text{NO}} + 2n_{\text{N}_2}$

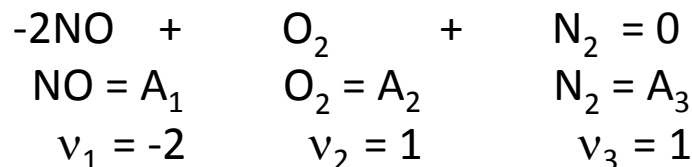
$$n_{\text{NO}}^o + 2n_{\text{O}_2}^o = n_{\text{NO}} + 2n_{\text{O}_2} \quad n_{\text{NO}}^o + 2n_{\text{N}_2}^o = n_{\text{NO}} + 2n_{\text{N}_2}$$

$$n_{\text{NO}} - n_{\text{NO}}^o = -2(n_{\text{O}_2} - n_{\text{O}_2}^o) \quad n_{\text{NO}} - n_{\text{NO}}^o = -2(n_{\text{N}_2} - n_{\text{N}_2}^o)$$

$$\frac{n_{\text{NO}} - n_{\text{NO}}^o}{-2} = \frac{(n_{\text{O}_2} - n_{\text{O}_2}^o)}{1} = \frac{(n_{\text{N}_2} - n_{\text{N}_2}^o)}{1}$$

Symbols for species

Stoichiometric coefficients



$$\sum_{i=1}^3 \nu_i A_i = 0$$

$\nu_i > 0$	products
$\nu_i = 0$	inerts
$\nu_i < 0$	reactants

Molar extent of the reaction

 ξ

[ksi:]

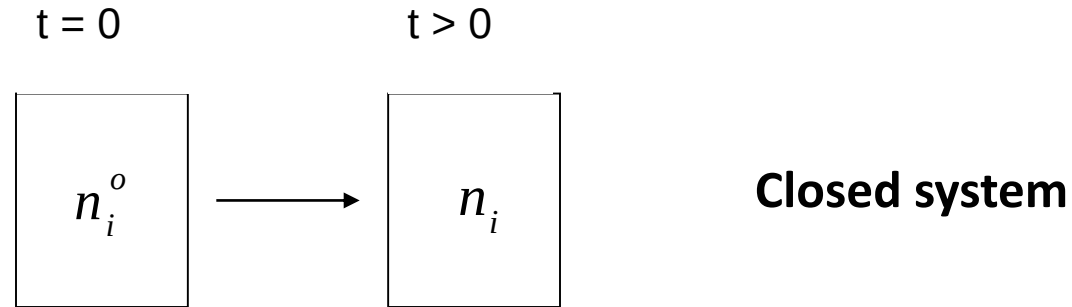
$$\xi = \frac{n_{NO} - n_{NO}^o}{-2} = \frac{(n_{O_2} - n_{O_2}^o)}{1} = \frac{(n_{N_2} - n_{N_2}^o)}{1}$$

$$\xi = \frac{n_i - n_i^o}{\nu_i}$$

From the definition of the reaction extent follows:

1. The reaction extent has the dimension of moles (number of molecules)
2. The reaction extent value depends on stoichiometry of reaction
3. The reaction extent is an extensive variable

Reaction extent for a single reaction in closed (batch) system



$\sum_{i=1}^N \nu_i A_i = 0$	$\nu_i > 0$	products
	$\nu_i = 0$	inerts
	$\nu_i < 0$	reactants

$$\xi = \frac{n_i - n_i^o}{\nu_i}$$

$$n_i = n_i^o + \nu_i \xi$$

Example



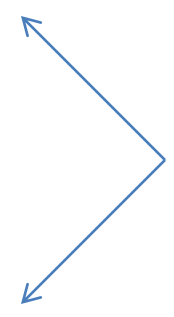
$$A_1 = \text{NO}, A_2 = \text{N}_2, A_3 = \text{O}_2$$

$$\nu_1 = -2, \nu_2 = 1, \nu_3 = 1$$

$$\mathbf{v}^T = (-2 \quad 1 \quad 1), \mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}$$

$$\mathbf{v}^T \mathbf{A} = (-2 \quad 1 \quad 1) \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} = 0$$

Matrix notation



Fractional conversion of key component, j

X_j

$$X_j = \frac{\xi}{\xi_{\max}}$$

$$\xi_{\max} = \frac{n_j^* - n_j^o}{\nu_j}$$

Number of moles of key component in limits (chemical equilibrium or 0)

$$n_j^* = 0$$

$$X_j = \frac{\xi}{\xi_{\max}} = \frac{\frac{\nu_i}{-n_j^o}}{\frac{\nu_j}{n_j^o}} = \frac{\nu_j}{\nu_i} \frac{n_i^o - n_i}{n_j^o}$$

$i = j$

$$X_j = \frac{n_j^o - n_j}{n_j^o} \quad X_j \in (0,1)$$

$$X_j = 100 \frac{n_j^o - n_j}{n_j^o} \quad X_j \in (0,100)$$

$$\xi = X_j \xi_{\max} = -X_j \frac{n_j^o}{\nu_j}$$

$$n_i = n_i^o - \frac{\nu_i}{\nu_j} n_j^o X_j$$

Stoichiometric matrix in the case of several reactions

$$\sum_{i=1}^N \nu_{ki} A_i = 0 \quad k = 1, NR$$

reaction $\nearrow$ component

Stoichiometric matrix has NR rows and N columns

$$\mathbf{v} = \begin{pmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1N} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{NR,1} & \nu_{NR,2} & \cdots & \nu_{NR,N} \end{pmatrix}, \mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix}$$

$$\mathbf{vA} = \mathbf{0}$$

Number of moles of i-th component consumed or created in k-th reaction :

$$n_{ki} - n_{ki}^o$$

Molar extent of k-th reaction :

$$\xi_k = \frac{n_{ki} - n_{ki}^o}{\nu_{ki}}$$

Number of moles of i-th components:

$$n_i = n_i^o + \sum_{k=1}^{NR} \nu_{ki} \xi_k$$

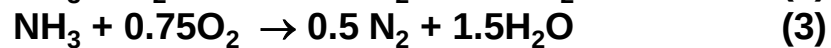
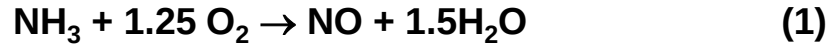
Matrix notation

$$\mathbf{n} = \mathbf{n}^o + \mathbf{v}^T \boldsymbol{\xi}$$

$$\mathbf{n} = \begin{pmatrix} n_1 \\ n_2 \\ \vdots \\ n_N \end{pmatrix}, \mathbf{n}^o = \begin{pmatrix} n_1^o \\ n_2^o \\ \vdots \\ n_N^o \end{pmatrix}, \boldsymbol{\xi} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_{NR} \end{pmatrix}$$

Problem 1.1

Oxidation of ammonia on Pt-Rh catalyst



Task: To write down the stoichiometric matrix.

	A_1	A_2	A_3	A_4	A_5	A_6
Reaction	NH_3	O_2	NO	N_2O	N_2	H_2O
(1)	-1	-1.25	1	0	0	1.5
(2)	-1	-1	0	0.5	0	1.5
(3)	-1	-0.75	0	0	0.5	1.5

Molar balance table of component in closed (batch) system

Component	$t = 0$	$t > 0$
NH_3	n_1^o	$n_1 = n_1^o - (\xi_1 + \xi_2 + \xi_3)$
O_2	n_2^o	$n_2 = n_2^o - 1.25\xi_1 - \xi_2 - 0.75\xi_3$
NO	n_3^o	$n_3 = n_3^o + \xi_1$
N_2O	n_4^o	$n_4 = n_4^o + 0.5\xi_2$
N_2	n_5^o	$n_5 = n_5^o + 0.5\xi_3$
H_2O	n_6^o	$n_6 = n_6^o + 1.5(\xi_1 + \xi_2 + \xi_3)$
Σ	$\sum_{i=1}^6 n_i^o$	$\sum_{i=1}^6 n_i^o + 0.25(\xi_1 + \xi_3)$

e.g. molar fraction of NH_3

$$y_1 = \frac{n_1^o - (\xi_1 + \xi_2 + \xi_3)}{\sum_{i=1}^6 n_i^o + 0.25(\xi_1 + \xi_3)}$$

Independent reactions

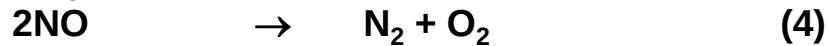
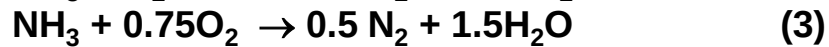
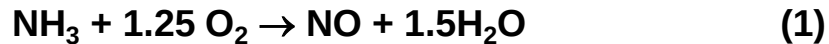
Set of NR reactions in reaction network is independent if

$$\text{Rank}(v) = \text{NR}$$

or

$$\text{number of independent reactions} = \text{Rank}(v)$$

Problem 1.2



Task: To calculate the number of independent reactions.

We determine the rank of stoichiometric matrix by Gaussian elimination:

$$\begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ -1 & -1 & 0 & 0.5 & 0 & 1.5 \\ -1 & -0.75 & 0 & 0 & 0.5 & 1.5 \\ 0 & 1 & -2 & 0 & 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0.5 & -1 & 0 & 0.5 & 0 \\ 0 & 1 & -2 & 0 & 1 & 0 \end{pmatrix} \rightarrow$$
$$\rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0.5 & 0 \\ 0 & 0 & 2 & -2 & 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0.5 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

**Rank(v)=3 → only 3 reactions
are independent**

Extent of the reaction in a flow system



$$\sum_{i=1}^N \nu_{ki} A_i = 0$$

$k = 1, NR$ **Open (flow) system in a steady state**

$$F_i = F_i^o + \sum_{k=1}^{NR} \nu_{ki} \dot{\xi}_k \quad \dot{\xi}_k = \frac{\xi_k}{\bar{\tau}}$$

F_i, F_i^o -outlet, inlet molar flow rates of i-th species [mole/s]

$\dot{\xi}_k$ – extent of k-th reaction per unit of time [mole/s]

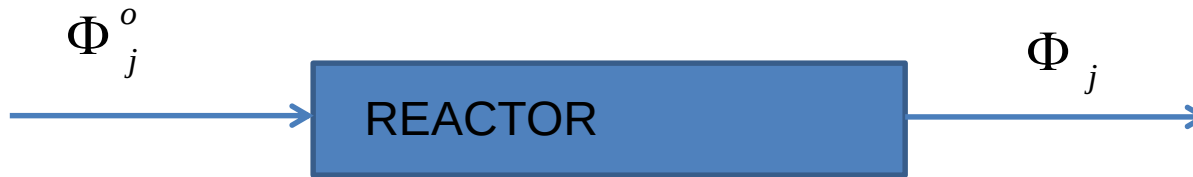
$\bar{\tau}$ – mean residence time [s]

$$\mathbf{F} = \mathbf{F}^o + \mathbf{v}^T \dot{\boldsymbol{\xi}}$$

$$\mathbf{F} = \begin{pmatrix} F_1 \\ F_2 \\ \vdots \\ F_N \end{pmatrix}, \mathbf{F}^o = \begin{pmatrix} F_1^o \\ F_2^o \\ \vdots \\ F_N^o \end{pmatrix}, \dot{\boldsymbol{\xi}} = \begin{pmatrix} \dot{\xi}_1 \\ \dot{\xi}_2 \\ \vdots \\ \dot{\xi}_{NR} \end{pmatrix}$$

A reaction is at steady-state if the concentration of all species in each element of the reaction space (i.e. volume in the case of homogeneous reaction or surface of catalyst in the case of catalytic heterogeneous reaction) does not change in time.

Balance of chemical elements



$$\sum_{i=1}^N \nu_{ki} A_i = 0 \quad k = 1, NR \quad \text{Open (flow) system at steady state}$$

$$\Phi_j = \Phi_j^o$$

Φ_j, Φ_j^o -outlet, inlet molar flows

of j-th chemical element [mole/s]

$$\Phi = \Phi^o$$

$$\Phi = \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \vdots \\ \Phi_{NEL} \end{pmatrix}, \Phi^o = \begin{pmatrix} \Phi_1^o \\ \Phi_2^o \\ \vdots \\ \Phi_{NEL}^o \end{pmatrix}$$

NEL - Number of
chemical elements

Formula matrix E

NEL elements → NEL=3

N components ↓ N=6	N	H	O
NH ₃	1	3	0
O ₂	0	0	2
NO	1	0	1
N ₂ O	2	0	1
N ₂	2	0	0
H ₂ O	0	2	1

Formula vector of NH₃

There are no creation or annihilation of chemical elements in chemical reactions:

$$\mathbf{vE} = \mathbf{0} \Rightarrow \begin{pmatrix} v_{11} & v_{12} & \dots & v_{1N} \\ v_{21} & v_{22} & \dots & v_{2N} \\ . & . & . & . \\ v_{NR,1} & v_{NR,2} & \dots & v_{NR,N} \end{pmatrix} \begin{pmatrix} E_{11} & E_{12} & \dots & E_{1,NEL} \\ E_{21} & \dots & \dots & E_{2,NEL} \\ . & . & . & . \\ E_{N,1} & E_{N,2} & \dots & E_{N,NEL} \end{pmatrix} = \underbrace{\begin{pmatrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ . & . & . & . \\ 0 & 0 & \dots & 0 \end{pmatrix}}_{\text{NEL}} \left. \vphantom{\begin{pmatrix} 0 & 0 & \dots & 0 \\ 0 & 0 & \dots & 0 \\ . & . & . & . \\ 0 & 0 & \dots & 0 \end{pmatrix}} \right\} \text{NR}$$

Molar* weight (relative molecular mass) of i-th species:

$$M_i = \sum_{j=1}^{NEL} E_{ij} m_j$$

$$\mathbf{M} = \mathbf{E} \mathbf{m}$$

Atomic weights (relative atomic mass) of j-th element

$$\mathbf{M} = \begin{pmatrix} M_1 \\ M_2 \\ \vdots \\ M_N \end{pmatrix}, \mathbf{m} = \begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_{NEL} \end{pmatrix}$$

and we have for molar weights of species

$$\mathbf{v} \mathbf{M} = \mathbf{v} \mathbf{E} \mathbf{m} = 0$$

$$\text{because } \mathbf{v} \mathbf{E} = 0$$

**The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12.*

Avogadro constant = $6.022\,141\,29(27) \times 10^{23} \text{ mol}^{-1}$

(<http://www.nist.gov>)



Balances of atoms in batch and flow systems

Closed (batch) system:

$$\mathbf{n} = \mathbf{n}^0 + \mathbf{v}^T \xi$$

$$\mathbf{E}^T \mathbf{n} = \mathbf{E}^T \mathbf{n}^0 + \mathbf{E}^T \mathbf{v}^T \xi = \mathbf{E}^T \mathbf{n}^0 + (\mathbf{vE})^T \xi = \mathbf{E}^T \mathbf{n}^0$$

Open (flow) system at steady state:

$$\mathbf{F} = \mathbf{F}^0 + \mathbf{v}^T \dot{\xi}$$

$$\mathbf{E}^T \mathbf{F} = \mathbf{E}^T \mathbf{F}^0 + \mathbf{E}^T \mathbf{v}^T \dot{\xi} = \mathbf{E}^T \mathbf{F}^0 + (\mathbf{vE})^T \dot{\xi} = \mathbf{E}^T \mathbf{F}^0$$

because $\mathbf{vE} = \mathbf{0}$

Finally

$$\mathbf{E}^T (\mathbf{n} - \mathbf{n}^0) = \mathbf{E}^T (\mathbf{n}^0 - \mathbf{n}) = \mathbf{0}$$

$$\mathbf{E}^T (\mathbf{F} - \mathbf{F}^0) = \mathbf{E}^T (\mathbf{F}^0 - \mathbf{F}) = \mathbf{0}$$

These equations are used in data reconciliation tasks around chemical reactors.

The last equation (flow system) is valid only at steady state.

Problem 1.3

Selective reduction of NO_x by C_3H_8



Steady state,
unknown
stoichiometry
of reactions

	NO	NO_2	CO	C_3H_8	CO_2	H_2O	O_2	N_2
$F_i^o [\mu\text{mole} / \text{min}]$	4.563	0.1845	0	2.943	0	0	90	0
$F_i [\mu\text{mole} / \text{min}]$	2.2905	2.3355	0	2.898	x	x	x	x

Calculate the missing outlet molar flow rates

$$\mathbf{E}^T (\mathbf{F}^o - \mathbf{F}) = \mathbf{E}^T \Delta \mathbf{F} = \mathbf{0}$$

	1-NO	2- NO_2	3-CO	4- C_3H_8	5- CO_2	6- H_2O	7- O_2	8- N_2
N	1	1	0	0	0	0	0	2
O	1	2	1	0	2	1	2	0
C	0	0	1	3	1	0	0	0
H	0	0	0	8	0	2	0	0

$$\mathbf{E}_1^T$$

$$\mathbf{E}_2^T$$

$$\begin{pmatrix} \Delta F_1 \\ \Delta F_2 \\ \Delta F_3 \\ \Delta F_4 \\ \Delta F_5 \\ \Delta F_6 \\ \Delta F_7 \\ \Delta F_8 \end{pmatrix} \begin{matrix} \text{known} \\ \Delta F_i \\ \text{unknown} \\ \Delta F_i \end{matrix}$$

$$\mathbf{E}_1^T \Delta \mathbf{F}_{\text{KNOWN}} + \mathbf{E}_2^T \Delta \mathbf{F}_{\text{UNKNOWN}} = \mathbf{0}$$

$$\mathbf{E}_2^T \Delta \mathbf{F}_{\text{UNKNOWN}} = -\mathbf{E}_1^T \Delta \mathbf{F}_{\text{KNOWN}}$$

$$\Delta \mathbf{F}_{\text{UNKNOWN}} = -(\mathbf{E}_2^T)^{-1} \mathbf{E}_1^T \Delta \mathbf{F}_{\text{KNOWN}} = \mathbf{Q} \Delta \mathbf{F}_{\text{KNOWN}}$$

$$\mathbf{Q} = -(\mathbf{E}_2^T)^{-1} \mathbf{E}_1^T$$

We obtain using Excel (**homework 1**)

$$\mathbf{Q} = \begin{pmatrix} 0 & 0 & -1 & -3 \\ 0 & 0 & 0 & -4 \\ -0.5 & -1 & 0.5 & 5 \\ -0.5 & -0.5 & 0 & 0 \end{pmatrix}$$

and taking $\Delta F_2 = -(\mathbf{E}_2^T)^{-1} \mathbf{E}_1^T \Delta F_1 = \mathbf{Q} \Delta F_1$ we have

	NO	NO ₂	CO	C ₃ H ₈	CO ₂	H ₂ O	O ₂	N ₂
$F_i^o [\mu mole / min]$	4.563	0.1845	0	2.943	0	0	90	0
$F_i [\mu mole / min]$	2.2905	2.3355	0	2.898	0.135	0.18	88.76	0.061

Selectivity

Moles of a particular product generated per mole of key reactant consumed

Yield

Moles of a particular product generated per one initial mole of key reactant

Ammonia oxidation

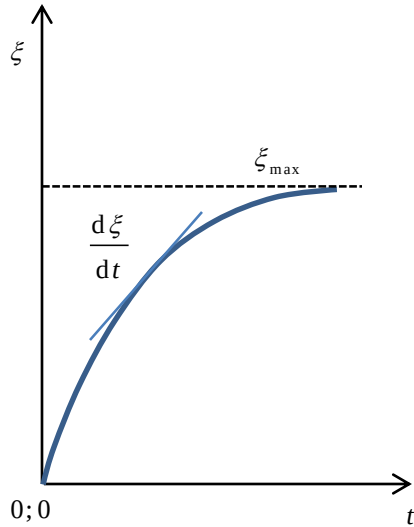
Component	$t = 0$	$t > 0$
NH_3	n_1^o	$n_1 = n_1^o - (\xi_1 + \xi_2 + \xi_3)$
O_2	n_2^o	$n_2 = n_2^o - 1.25\xi_1 - \xi_2 - 0.75\xi_3$
NO	n_3^o	$n_3 = n_3^o + \xi_1$
N_2O	n_4^o	$n_4 = n_4^o + 0.5\xi_2$
N_2	n_5^o	$n_5 = n_5^o + 0.5\xi_3$
H_2O	n_6^o	$n_6 = n_6^o + 1.5(\xi_1 + \xi_2 + \xi_3)$

$$S_{\text{NO}-\text{NH}_3} = \frac{n_3^o + \xi_1}{(\xi_1 + \xi_2 + \xi_3)} = \frac{\xi_1}{(\xi_1 + \xi_2 + \xi_3)}$$

$$Y_{\text{NO}-\text{NH}_3} = \frac{n_3^o + \xi_1}{n_1^o} \stackrel{(n_3^o=0)}{=} \frac{\xi_1}{n_1^o}$$

Reaction rate

(IUPAC Gold Book = rate of conversion)



$$r = \frac{d\xi}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.s}^{-1}$$

$$r_k = \frac{d\xi_k}{dt}$$

Closed system
of uniform
pressure,
temperature
and
composition.

Rate of generation (consumption) of component A_i

$$R_{A_i} = \frac{dn_i}{dt} = \nu_i \cdot \frac{d\xi}{dt} = \nu_i \cdot r$$

one reaction

$\Rightarrow$

$$\mathbf{R} = \mathbf{v}r$$

$$R_{A_i} = \sum_{k=1}^{NR} \nu_{ki} \cdot \frac{d\xi_k}{dt} = \sum_{k=1}^{NR} \nu_{ki} \cdot r_k$$

several reactions

$\Rightarrow$

$$\mathbf{R} = \mathbf{v}^T \mathbf{r}$$

We measure usually the rates of generation (consumption) of components R and we want to calculate r

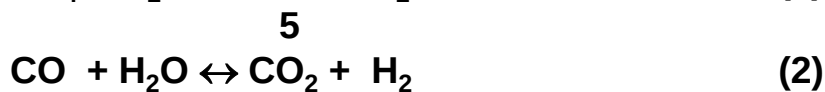
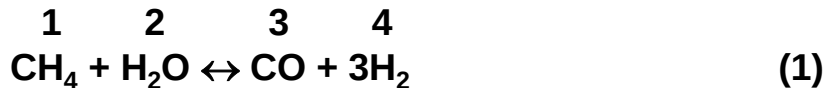
$$\mathbf{R}^{\text{exp}} \cong \mathbf{v}^T \mathbf{r} \quad \Rightarrow \quad \text{Objective function} \quad \Omega(\mathbf{r}) = \left(\mathbf{R}^{\text{exp}} - \mathbf{v}^T \mathbf{r} \right)^T \left(\mathbf{R}^{\text{exp}} - \mathbf{v}^T \mathbf{r} \right)$$

minimization of $\Omega(\mathbf{r})$ = least squares solution of overdefined system ($N > NR$)

$$\mathbf{r} = \left(\mathbf{v} \mathbf{v}^T \right)^{-1} \mathbf{v} \mathbf{R}^{\text{exp}}$$

Problem 1.4

Steam reforming of methane (5 species, $N=5$, 2 reactions, $NR=2$)



Measured $\mathbf{R}$: $(-0.97572, -2.88778, -1.02127, 4.832804, 2.078537)^T$ (mol/s)

$$\mathbf{v} = \begin{pmatrix} -1 & -1 & 1 & 3 & 0 \\ 0 & -1 & -1 & 1 & 1 \end{pmatrix} \quad \mathbf{v} \mathbf{v}^T = \begin{pmatrix} 12 & 3 \\ 3 & 4 \end{pmatrix} \quad \left(\mathbf{v} \mathbf{v}^T \right)^{-1} \mathbf{v} = \begin{pmatrix} -0.10256 & -0.02564 & 0.179487 & 0.230769 & -0.07692 \\ 0.076923 & -0.23077 & -0.38462 & 0.076923 & 0.307692 \end{pmatrix}$$

$$\begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} 0.94619 \\ 1.99546 \end{pmatrix}$$

Specific reaction rate

The reaction rate $\frac{d\xi}{dt}$ is, like ξ , an extensive property of the system, a specific rate (intensive property) is obtained by dividing $\frac{d\xi}{dt}$ by the total volume, mass, surface of the system:

Reaction rate per volume

$$r_V = \frac{1}{V} r = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{V} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.m}^{-3}.\text{s}^{-1}$$

$$r_{V,k} = \frac{1}{V} r_k = \frac{1}{V} \frac{d\xi_k}{dt}$$

Reaction rate per mass

$$r_M = \frac{1}{m} r = \frac{1}{m} \frac{d\xi}{dt} = \frac{1}{m} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.kg}^{-1}.\text{s}^{-1}$$

$$r_{M,k} = \frac{1}{m} r_k = \frac{1}{m} \frac{d\xi_k}{dt}$$

Reaction rate per surface

$$r_s = \frac{1}{S} r = \frac{1}{S} \frac{d\xi}{dt} = \frac{1}{S} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.m}^{-2}.\text{s}^{-1}$$

$$r_{s,k} = \frac{1}{S} r_k = \frac{1}{S} \frac{d\xi_k}{dt}$$

Reaction rate per active center (turnover number)

$$r_{RS} = \frac{1}{n_{RS}} r = \frac{1}{n_{RS}} \frac{d\xi}{dt} = \frac{1}{n_{RS}} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{s}^{-1}$$

$$r_{RS,k} = \frac{1}{n_{RS}} r_k = \frac{1}{n_{RS}} \frac{d\xi_k}{dt}$$

Central problem of APPLIED CHEMICAL KINETICS

$r = \text{function}(T, c_1, c_2, \dots, c_N, P, \text{catalytic activity, transport parameters, } \dots)$

Rule 1: The rate function r at constant temperature generally decreases in monotonic fashion with time (or extent or conversion).

Rule 2: The rate of irreversible reaction can be written as

$$r = k(T)g(c_1, c_2, \dots, c_N)$$

Rule 3: The rate constant k depends on temperature (Svante Arrhenius, 1889):

$$k(T) = Ae^{-\frac{E}{RT}}$$

Rule 4: The function g is independent of temperature:

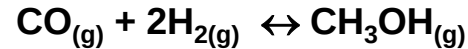
$$g(c_1, c_2, \dots, c_N) = c_1^{\alpha_1} c_2^{\alpha_2} \dots c_N^{\alpha_N} = \prod_{i=1}^N c_i^{\alpha_i}$$

Rule 5: When a reaction is reversible:

$$r = r_f - r_b = k_f(T)g_f(c_1, c_2, \dots, c_N) - k_b(T)g_b(c_1, c_2, \dots, c_N)$$

Problem 1.5 (homework 2)

In flow catalytic reactor the synthesis of methanol is carried out



The inlet mass flow rate of CO is 1000 kg.h^{-1} of CO and the inlet flow rate of hydrogen is supplied so that the inlet molar ratio $\text{H}_2:\text{CO}$ is equal to 2:1. 1200 kg of the catalyst is placed in the reactor.

The outlet mass flow of CO is 860 kg.h^{-1} .

To determine:

1. Mean reaction rate per mass of catalyst in $\text{mol.kg}^{-1}.\text{s}^{-1}$.
2. If specific internal surface of catalyst is $55 \text{ m}^2.\text{g}^{-1}$, calculate mean reaction rate per surface of catalyst in $\text{mol.m}^{-2}.\text{s}^{-1}$.
3. If per 1 m^2 of catalyst contains 10^{19} active sites, calculate mean reaction rate per active site in s^{-1} .
4. Calculate inlet and outlet gas mixture composition in molar fractions.

Data:

$$M_{\text{CO}} = 28.010 \text{ kg.kmol}^{-1}$$

$$N_A = 6.0221413 \times 10^{23} \text{ mol}^{-1} \text{ (Avogadro number)}$$

$$CO = A_1, H_2 = A_2, CH_3OH = A_3$$

$$\mathbf{v} = \begin{pmatrix} -1 \\ -2 \\ 1 \end{pmatrix}, \mathbf{R} = \begin{pmatrix} -1 \\ -2 \\ 1 \end{pmatrix} r$$

$$F_i = F_i^o + \sum_{k=1}^{NR} \nu_{ki} \dot{\xi}_k \Rightarrow F_i = F_i^o + \nu_i \dot{\xi} \Rightarrow$$

$$\bar{r}_M = \frac{\dot{\xi}}{m_{CAT}} = \frac{F_i - F_i^o}{\nu_i m_{CAT}}, \bar{r}_S = \frac{\dot{\xi}}{S} = \frac{F_i - F_i^o}{\nu_i S}, \bar{r}_{RS} = \frac{\dot{\xi}}{n_{RS}} = \frac{F_i - F_i^o}{\nu_i n_{RS}}$$

Fractional conversion of key component

1 = key component

$$X_1 = \frac{\dot{\xi}}{\dot{\xi}_{MAX}} = \left(\frac{F_i - F_i^o}{\nu_i} \right) / \left(\frac{-F_1^o}{\nu_1} \right) \Rightarrow F_i = F_i^o - \frac{\nu_i}{\nu_1} F_1^o X_1$$

	inlet	y_i^o	outlet	y_i	
1-CO	F_1^o	$y_1^o = \frac{F_1^o}{3F_1^o} = \frac{1}{3}$	$F_1 = F_1^o + (-1)\dot{\xi}$	$y_1 = \frac{F_1^o + (-1)\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_1 = F_1^o (1 - X_1)$
2-H2	$2F_1^o$	$y_2^o = \frac{2F_1^o}{3F_1^o} = \frac{2}{3}$	$F_2 = F_2^o + (-2)\dot{\xi}$	$y_2 = \frac{2F_1^o + (-2)\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_2 = 2F_1^o - 2F_1^o X_1$
3-CH3OH	0	0	$F_3 = F_3^o + (+1)\dot{\xi}$	$y_3 = \frac{\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_3 = F_1^o X_1$
Σ	$F^o = 3F_1^o$	1	$F = F^o + (-2)\dot{\xi}$	1	$F = 3F_1^o - 2F_1^o X_1$

$$i=1, \dot{\xi} = \frac{(860 - 1000) / 0.02801 / 3600}{-1} = 1.38839 \text{ mol.s}^{-1}$$

$$\bar{r}_M = \frac{1.38839}{1200} = 1.157 \times 10^{-3} \text{ mol.kg}^{-1} \cdot \text{s}^{-1}, \bar{r}_S = \frac{1.38839}{55 \times 10^3 \times 1200} = 2.104 \times 10^{-8} \text{ mol.m}^{-2} \cdot \text{s}^{-1}$$

$$\bar{r}_{RS} = \frac{1.38839 \times 6.0221413 \times 10^{23}}{55 \times 10^3 \times 1200 \times 10^{19}} = 1.267 \times 10^{-3} \text{ s}^{-1}$$

$$X_1 = \frac{(1000 - 860)}{1000} = 0.14$$

	inlet y_i^o	outlet y_i
1-CO	$y_1^o = \frac{F_1^o}{3F_1^o} = \frac{1}{3}$	$y_1 = \frac{F_1^o(1 - X_1)}{3F_1^o - 2F_1^o X_1} = \frac{1 - X_1}{3 - 2X_1} = 0.3162$
2-H ₂	$y_2^o = \frac{2F_1^o}{3F_1^o} = \frac{2}{3}$	$y_2 = \frac{2F_1^o - 2F_1^o X_1}{3F_1^o - 2F_1^o X_1} = \frac{2(1 - X_1)}{3 - 2X_1} = 0.6324$
3-CH ₃ OH	0	$y_3 = \frac{F_1^o X_1}{3F_1^o - 2F_1^o X_1} = \frac{X_1}{3 - 2X_1} = 0.05147$
Σ	1	1

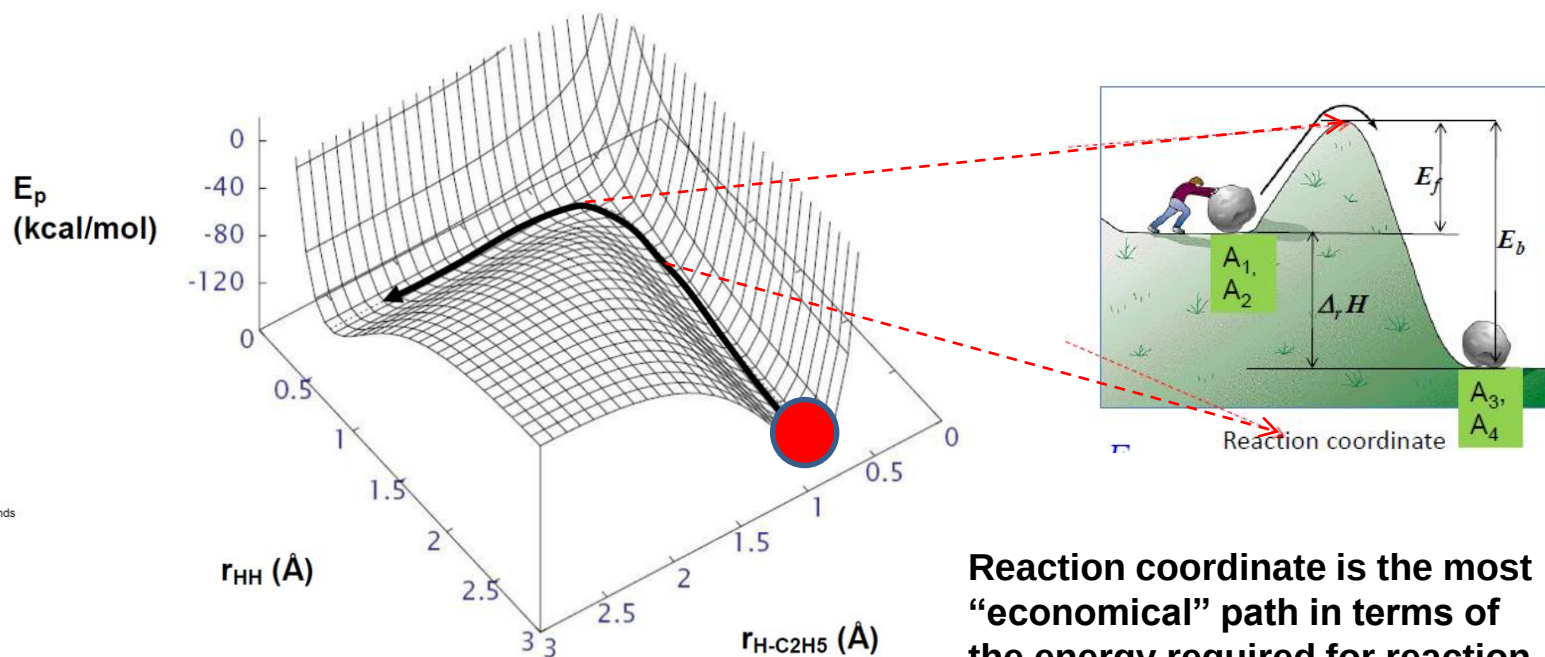
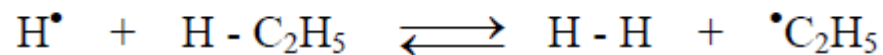
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2. Elementary reaction. Transition state theory.

- The rearrangement of atoms occurs through the motion of nuclei in the continuous potential field set up by the rapid motion of the electrons of the system.
- For the elementary reaction there exists a single potential energy surface on which the system will move to go from reactants to products and back, e.g.



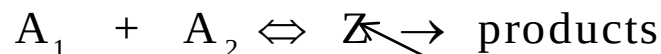
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Transition State Theory = Theory of absolute reaction rates

(S. Glasstone, K.J. Laidler, H. Eyring, 1941)



Transition state (Activated complex) in equilibrium with reactants

$$r_v = f_o c_z$$

$$f_o = \frac{k_B T}{h} \quad \text{characteristic frequency of activated complex decomposition}$$

$$f_o(500\text{K}) \cong 10^{13} \text{ s}^{-1}$$

kinetic equation (see next slide)

$$r_v = A_o \cdot \exp\left(-\frac{E}{RT}\right) \cdot c_{A_1} c_{A_2}$$

$$k_B = 1,38054 \cdot 10^{-23} \text{ J.K}^{-1} \text{ (Boltzmann's constant)}$$

$$h = 6,6256 \cdot 10^{-34} \text{ J.s (Planck's constant)}$$

Justification of kinetic equation

$$K_Z^{eq} = \frac{a_Z}{a_{A_1} a_{A_2}} = \frac{\gamma_Z}{\gamma_{A_1} \gamma_{A_2}} \frac{c_Z}{c_{A_1} c_{A_2}}$$

$$\exp \left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R} \right] = \frac{\gamma_Z}{\gamma_{A_1} \gamma_{A_2}} \frac{c_Z}{c_{A_1} c_{A_2}}$$

$$c_Z = \underbrace{\frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_Z} \exp \left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R} \right]}_{\text{}} c_{A_1} c_{A_2}$$

$$r_V = \frac{k_B T}{h} c_Z = \frac{k_B T}{h} \frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_Z} \exp \left[-\frac{\Delta H_Z^o}{RT} + \frac{\Delta S_Z^o}{R} \right] c_{A_1} c_{A_2}$$

$$r_V = A_o \cdot \exp \left(-\frac{E}{RT} \right) \cdot c_{A_1} c_{A_2}$$

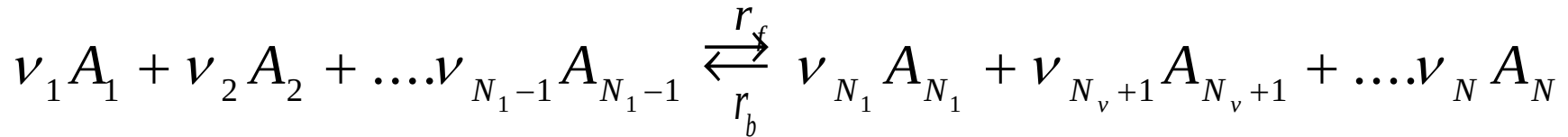
$$A_o = \frac{k_B T}{h} \exp \left[\frac{\Delta S_Z^o}{R} \right] \frac{\gamma_{A_1} \gamma_{A_2}}{\gamma_Z}, \quad E = \Delta H_Z^o$$

$E = \Delta H_Z^o$ – standard enthalpy of active complex formation (J.mol⁻¹)

ΔS_Z^o – standard entropy of active complex formation (J.mol⁻¹.K⁻¹)

$\gamma_{A_1}, \gamma_{A_2}, \gamma_Z$ – activity coefficients of reactants and activated complex, resp.

Kinetics and thermodynamic equilibrium of elementary reaction



$A_1, A_2, \dots, A_{N_1-1}$ – reactants $A_{N_1}, A_2, \dots, A_N$ – products

$$r = r_f - r_b = k_f \prod_{i=1}^{N_1-1} c_i^{m_{f,i}} - k_b \prod_{j=N_1}^N c_j^{m_{b,j}} =$$

$$= \underbrace{A_{of} \cdot T^{n_1} \cdot \exp\left(-\frac{E_f}{RT}\right)}_{k_f} \prod_{i=1}^{N_1-1} c_i^{\underbrace{m_{f,i}}_{\text{order of reaction relative to component } i}} - \underbrace{A_{ob} \cdot T^{n_2} \cdot \exp\left(-\frac{E_b}{RT}\right)}_{k_b} \prod_{j=N_1}^N c_j^{\underbrace{m_{b,j}}_{\text{order of reaction relative to component } j}}$$

The orders of reaction relative to given component

In the thermodynamic equilibrium:

$$r = 0$$

$$r_f = r_b$$

$$A_{of} \cdot T^{n_1} \cdot \exp\left(-\frac{E_f}{RT}\right) \cdot \prod_{i=1}^{N_1-1} c_{i,eq}^{m_{f,i}} = A_{ob} \cdot T^{n_2} \cdot \exp\left(-\frac{E_b}{RT}\right) \cdot \prod_{j=N_1}^N c_{j,eq}^{m_{b,j}}$$

$$\frac{k_f}{k_b} = \frac{A_{of} \cdot T^{n_1}}{A_{ob} \cdot T^{n_2}} \exp\left[-\frac{(E_f - E_b)}{RT}\right] \cong \frac{A_{of}}{A_{ob}} \exp\left[-\frac{(E_f - E_b)}{RT}\right] = \frac{\prod_{j=N_1}^N c_{j,eq}^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{m_{f,i}}}$$

From classical thermodynamics it follows:

$$K_{eq} = \frac{\prod_{j=N_1}^N c_{j,eq}^{\nu_j}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{| \nu_i |}} = \exp\left(\frac{-\Delta_r G^o}{RT}\right) = \exp\left(\frac{-[\Delta_r H^o - T \Delta_r S^o]}{RT}\right) = \exp\left(\frac{\Delta_r S^o}{R}\right) \exp\left(\frac{-\Delta_r H^o}{RT}\right)$$

$$\frac{\prod_{j=N_1}^N c_{j,eq}^{\nu_j}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{| \nu_i |}} = \exp\left(\frac{\Delta_r S^o}{R}\right) \exp\left(\frac{-\Delta_r H^o}{RT}\right)$$

By comparison of kinetic and thermodynamic expressions:

$$K_{eq} = \frac{k_f}{k_b} \Rightarrow \frac{\prod_{j=N_1}^N c_{j,eq}^{\nu_j}}{\prod_{i=1}^{N_1-1} c_{i,eq}^{| \nu_i |}} = \frac{\prod_{j=N_v}^N c_{j,eq}^{m_{b,j}}}{\prod_{i=1}^{N_v-1} c_{i,eq}^{m_{f,i}}} \Rightarrow \begin{matrix} m_{b,j} = \nu_j \\ m_{f,i} = | \nu_i | \end{matrix} \Rightarrow \begin{matrix} \frac{A_{of}}{A_{ob}} = \exp\left(\frac{\Delta_r S^o}{R}\right) \\ E_f - E_b = \Delta_r H^o \end{matrix}$$

Using above developed relations , we get :

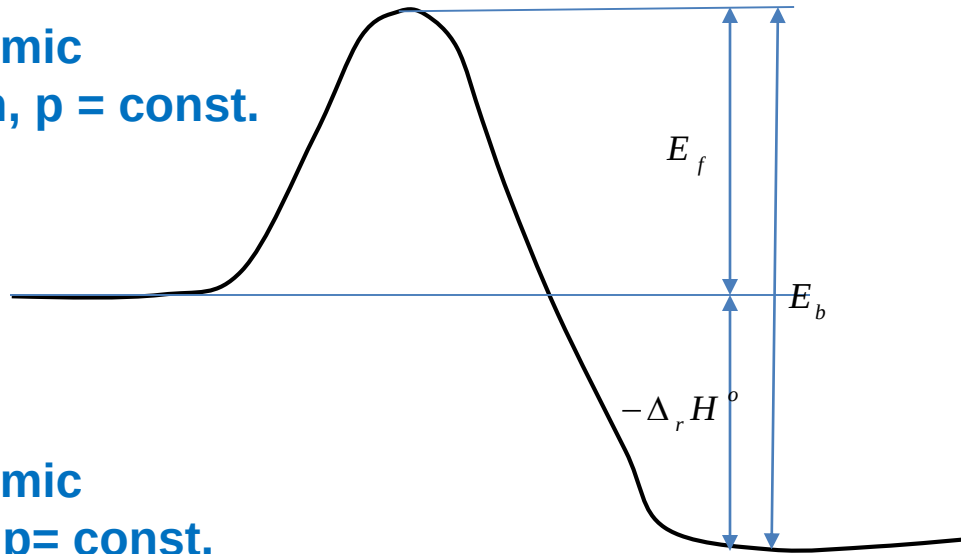
$$\begin{aligned}
 r &= r_f - r_b = k_f \prod_{i=1}^{N_1-1} c_i^{m_{f,i}} - k_b \prod_{j=N_1}^N c_j^{m_{b,j}} = k_f \left[\prod_{i=1}^{N_1-1} c_i^{m_{f,i}} - \frac{1}{K_{eq}} \prod_{j=N_1}^N c_j^{m_{b,j}} \right] = \\
 &= r_f \left[1 - \frac{1}{K_{eq}} \frac{\prod_{j=N_1}^N c_j^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_i^{m_{f,i}}} \right] = r_f [1 - \beta] \qquad \beta = \frac{1}{K_{eq}} \frac{\prod_{j=N_1}^N c_j^{m_{b,j}}}{\prod_{i=1}^{N_1-1} c_i^{m_{f,i}}}
 \end{aligned}$$

In the thermodynamic equilibrium

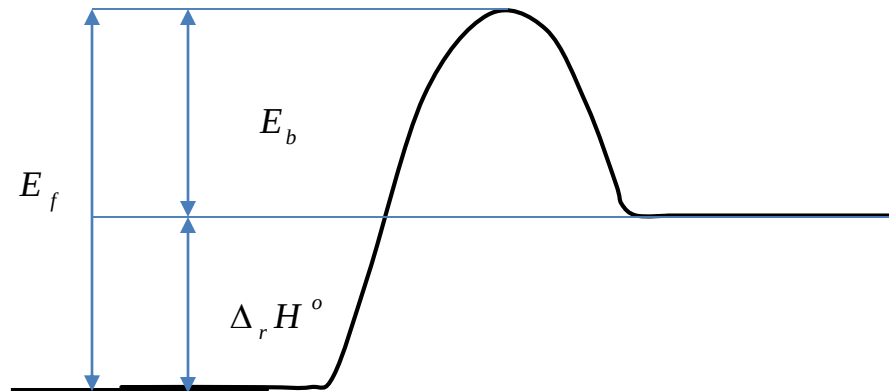
$$\beta \rightarrow 1 \Rightarrow r \rightarrow 0$$

Elementary reactions energy diagrams

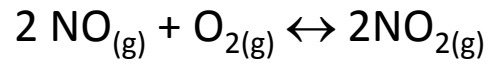
Exothermic
reaction, $p = \text{const.}$



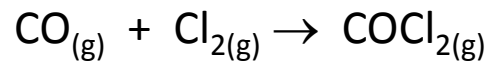
Endothermic
reaction, $p = \text{const.}$



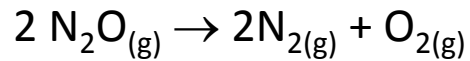
Examples of complex reactions



$$r_V = k_1 c_{\text{NO}}^2 c_{\text{O}_2} - k_2 c_{\text{NO}_2}^2$$



$$r_V = k c_{\text{CO}} c_{\text{Cl}_2}^{\frac{3}{2}}$$



$$r_S = \frac{k_1 c_{\text{N}_2\text{O}}}{1 + k_2 c_{\text{O}_2}}$$

3. Systems of reactions. Reversible, parallel, consecutive reactions. Complex reaction systems.



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Summary

- Simple systems of elementary reactions
- Open x Closed sequence of elementary steps
- Quasi Steady State Hypothesis
- Practically important examples

Elementary (one step) reactions between stable molecules are very rare. Rather, a sequence of elementary steps is necessary.

Examples

- Polymerization
- Catalytic and enzymatic reactions
- Combustion
- Catalytic reactions (homogeneous, heterogeneous)

Basic characteristics

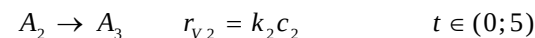
- large number of species ($N > 10^6$)
- complex mechanism
- effect of environment (e.g. effect of solid surface on reaction rate)
- highly exothermic or endothermic processes

Basic types of complex reactions

- 1) Reversible reactions
- 2) Parallel reactions
- 3) Consecutive reactions

Homework 3

To find $c_1(t)$, $c_2(t)$, $c_3(t)$ in the closed isotherm constant volume reaction system, in which the first order irreversible consecutive reactions take place

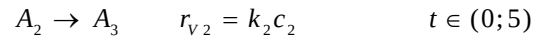


$$a) k_1 = 2 \text{ min}^{-1}, k_2 = 1 \text{ min}^{-1}$$

$$b) k_1 = k_2 = 1 \text{ min}^{-1}$$

$$c) t_{opt} \text{ for } c_2$$

HW 3



$$a) k_1 = 2 \text{ min}^{-1}, k_2 = 1 \text{ min}^{-1}$$

$$b) k_1 = k_2 = 1 \text{ min}^{-1}$$

$$c) t_{opt} \text{ for } c_2$$

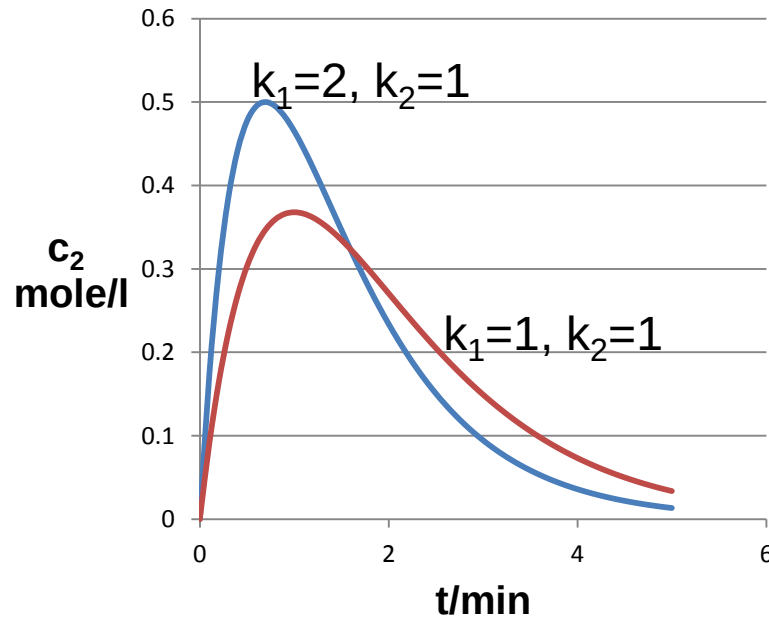
Solution

$$a) c_2 = c_1^o \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$b) c_2 = c_1^o k_1 t e^{-k_1 t}$$

$$c) k_1 \neq k_2, t_{opt} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1} = 0.693, c_2(t_{opt}) = c_1^o \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}} = \frac{1}{2} \text{ mol/l}$$

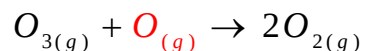
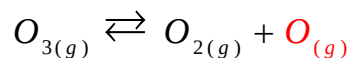
$$k_1 = k_2, t_{opt} = \frac{1}{k_1} = 1, c_2(t_{opt}) = \frac{c_1^o}{e} = 0.368 \text{ mol/l}$$

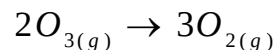


LINEAR 1ST ORDER DIFFERENTIAL
EQUATION ➡ INTEGRATION FACTOR

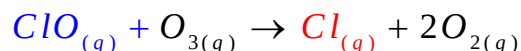
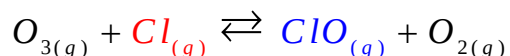
Open x Closed sequence of elementary steps

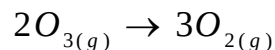
- In the sequence of elementary steps, the reactants and products of these are not stable reactants or products but are highly reactive intermediates.
- The reactive intermediates can be of several different chemical types : free radicals, free ions, solvated ions, complexes at solid surfaces, complexes in homogeneous phase, complexes with enzymes.
- Many intermediates may be involved in a given reaction, however the advancement of the reaction can still be described by means of a single parameter – extent of reaction or fractional conversion of key component.
- There are two types of sequences leading from reactants to products through intermediates: OPEN or CLOSED.
- An open sequence is one in which an intermediate is not reproduced in any other step of the sequence.
- A closed sequence is one in which an intermediate is reproduced so that a cyclic reaction pattern repeats itself and a large number of molecules of products can be made through only one intermediate. (Catalysis)





Open





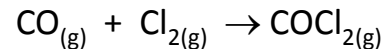
Closed
(catalytic)

Quasi Steady State Hypothesis – QSSH

The concentrations of the intermediates remain low and constant → these intermediate concentrations can be expressed using reactant and product concentrations

Example

Fosgen (COCl_2) is manufactured by gas phase reaction between CO and Cl_2



It follows from experimental data :

$$r_V = k c_{\text{CO}} c_{\text{Cl}_2}^{3/2} \quad [\text{mol.m}^{-3}.\text{s}^{-1}]$$

The proposed mechanism involves 2 intermediates **Cl** and **COCl**.

Reaction	Kinetic equation
1. $\text{Cl}_{2(g)} \leftrightarrow 2\text{Cl}_{(g)}$	$r_1 = k_{f,1} c_{\text{Cl}_2} - k_{b,1} c_{\text{Cl}}^2$
2. $\text{CO}_{(g)} + \text{Cl}_{(g)} \leftrightarrow \text{COCl}_{(g)}$	$r_2 = k_{f,2} c_{\text{CO}} c_{\text{Cl}} - k_{b,2} c_{\text{COCl}}$
3. $\text{COCl}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{COCl}_{2(g)} + \text{Cl}_{(g)}$	$r_3 = k_{f,3} c_{\text{COCl}} c_{\text{Cl}_2}$

The balances of intermediates at steady state:

$$R_{Cl} = 2r_1 - r_2 + r_3 = 0$$

$$R_{COCl} = r_2 - r_3 = 0$$

$$\mathbf{v} = \begin{matrix} & \text{Cl}_2 & \text{Cl} & \text{CO} & \text{COCl} & \text{COCl}_2 \\ \begin{pmatrix} -1 & 2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 0 \\ -1 & 1 & 0 & -1 & 1 \end{pmatrix} \end{matrix}$$

By adding above equations

$$2r_1 = 0 = r_1 = k_{f,1}c_{Cl_2} - k_{b,1}c_{Cl}^2$$

$$c_{Cl} = \left(\frac{k_{f,1}}{k_{b,1}} c_{Cl_2} \right)^{1/2}$$

Concentration of COCl:

$$R_{COCl} = r_2 - r_3 = k_{f,2}c_{CO}c_{Cl} - k_{b,2}c_{COCl} - k_{f,3}c_{COCl}c_{Cl_2} = 0$$

$$c_{COCl} = \frac{k_{f,2}c_{CO}c_{Cl}}{k_{b,2} + k_{f,3}c_{Cl_2}} = \frac{k_{f,2}c_{CO} \left(\frac{k_{f,1}}{k_{b,1}} c_{Cl_2} \right)^{1/2}}{k_{b,2} + k_{f,3}c_{Cl_2}} = \frac{k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} c_{CO} (c_{Cl_2})^{1/2}}{k_{b,2} + k_{f,3}c_{Cl_2}}$$

Rate of COCl_2 production is given by equation (3) in which we substitute for COCl concentration

$$R_{\text{COCl}_2} = r_3 = k_{f,3} c_{\text{COCl}} c_{\text{Cl}_2} = \frac{k_{f,3} k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} c_{\text{CO}} (c_{\text{Cl}_2})^{3/2}}{k_{b,2} + k_{f,3} c_{\text{Cl}_2}}$$

If Cl_2 concentration is low or $k_{b,2} \gg k_{f,3}$ is valid, we get

$$R_{\text{COCl}_2} = \frac{k_{f,3} k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2}}{k_{b,2}} c_{\text{CO}} (c_{\text{Cl}_2})^{3/2} = k c_{\text{CO}} (c_{\text{Cl}_2})^{3/2}$$

$$k = \frac{k_{f,3} k_{f,2} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2}}{k_{b,2}}$$

Validity of QSSH

$\text{Cl}_{2(g)} \leftrightarrow 2\text{Cl}_{(g)}$	$r_{V,1} = k_{f,1}c_{\text{Cl}_2} - k_{b,1}c_{\text{Cl}}^2$
$\text{CO}_{(g)} + \text{Cl}_{(g)} \leftrightarrow \text{COCl}_{(g)}$	$r_{V,2} = k_{f,2}c_{\text{CO}}c_{\text{Cl}} - k_{b,2}c_{\text{COCl}}$
$\text{COCl}_{(g)} + \text{Cl}_{2(g)} \rightarrow \text{COCl}_{2(g)} + \text{Cl}_{(g)}$	$r_{V,3} = k_{f,3}c_{\text{COCl}}c_{\text{Cl}_2}$

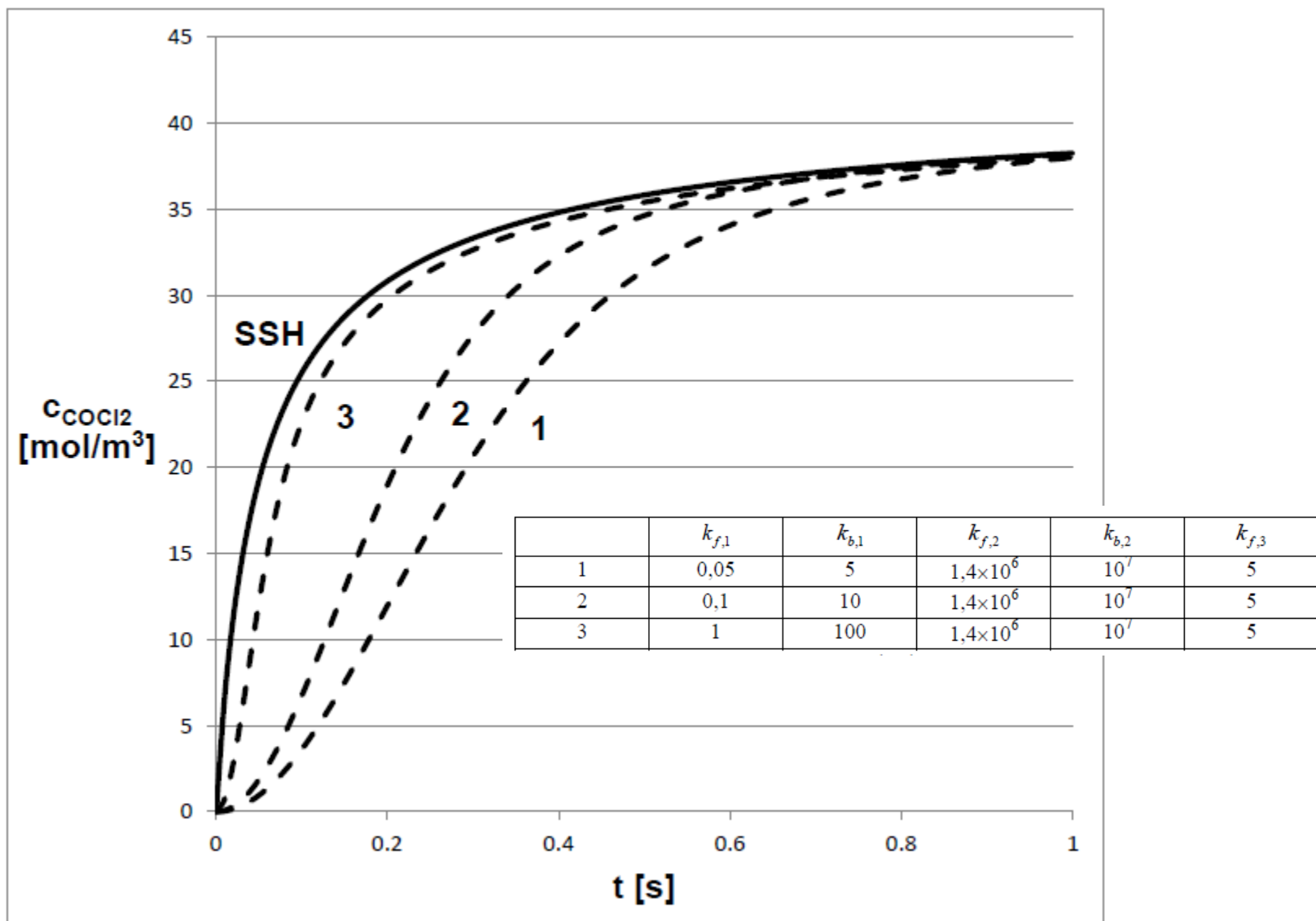
Isothermal batch constant volume reactor

$$\begin{aligned}\frac{dc_{\text{Cl}_2}}{dt} &= -r_{V,1} - r_{V,3} \\ \frac{dc_{\text{Cl}}}{dt} &= 2r_{V,1} - r_{V,2} + r_{V,3} \\ \frac{dc_{\text{CO}}}{dt} &= -r_{V,2} \\ \frac{dc_{\text{COCl}}}{dt} &= r_{V,2} - r_{V,3} \\ \frac{dc_{\text{COCl}_2}}{dt} &= r_{V,3}\end{aligned}$$

$$k = \frac{k_{f,3}k_{f,2}}{k_{b,2}} \left(\frac{k_{f,1}}{k_{b,1}} \right)^{1/2} = 0.07 \text{ (m}^3\text{mol}^{-1})^{3/2}\text{s}^{-1}$$

Kinetic parameters used in numerical simulation

	$k_{f,1}$	$k_{b,1}$	$k_{f,2}$	$k_{b,2}$	$k_{f,3}$
1	0,05	5	$1,4 \times 10^6$	10^7	5
2	0,1	10	$1,4 \times 10^6$	10^7	5
3	1	100	$1,4 \times 10^6$	10^7	5



Concentration profiles of COCl_2

Homework 4 (due after Chapter 4)

Calculate volumes of CSTR a PFR working at 150 °C and 300 kPa to produce 1 t COCl₂/day with CO conversion equal to 95 %. A mixture of CO and Cl₂ (molar ratio 1:1) is fed at 300 kPa and 150 °C.

Data

$$k(423 \text{ K}) = 0.07 \text{ (m}^3\text{mol}^{-1})^{3/2}\cdot\text{s}^{-1}$$

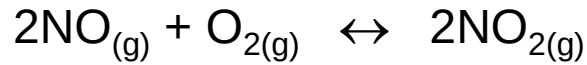
$$M_{\text{COCl}_2} = 98.92 \text{ kg/kmol.}$$

Answer:

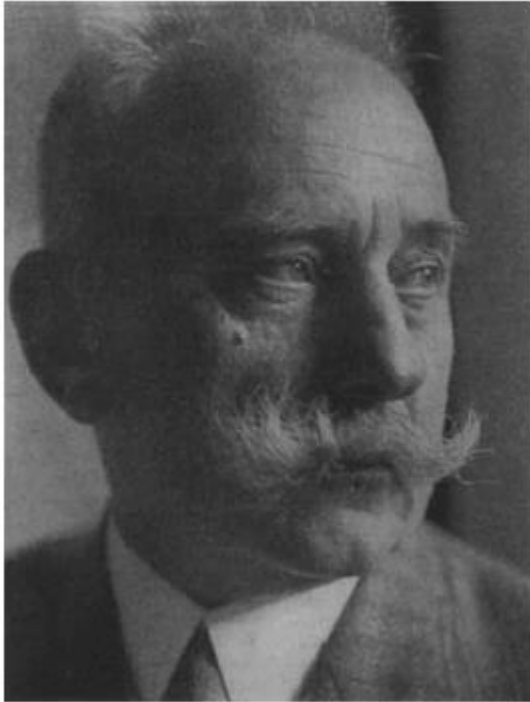
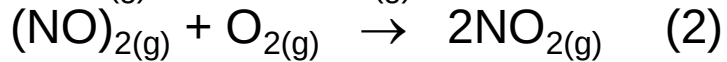
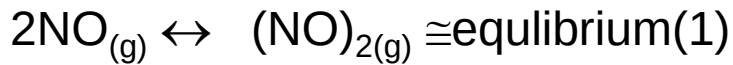
$$V_{\text{CSTR}} = 0.053 \text{ m}^3$$

$$V_{\text{PFR}} = 0.0021 \text{ m}^3$$

Example



Mechanism:



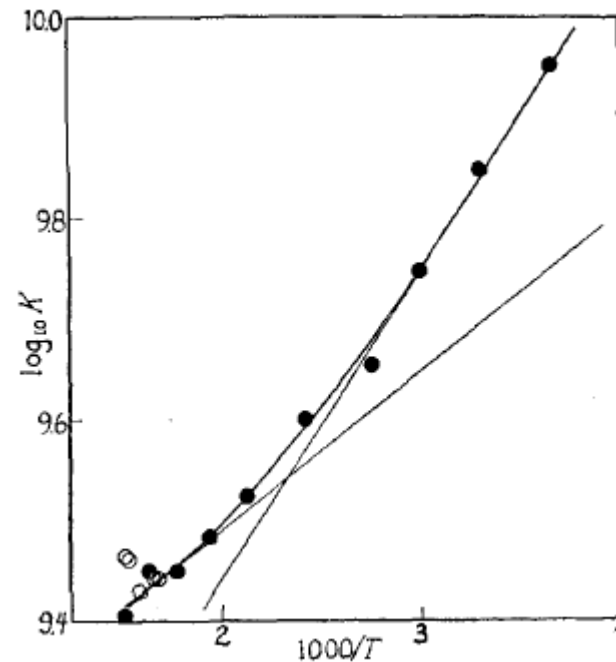
Max Bodenstein, 1941

$$K_1 = \frac{c_{(\text{NO})_2}}{c_{\text{NO}}^2}$$

$$r_2 = k_{f,2} c_{(\text{NO})_2} c_{\text{O}_2} - k_{b,2} c_{\text{NO}_2}^2 = k_{f,2} K_1 c_{\text{NO}}^2 c_{\text{O}_2} - k_{b,2} c_{\text{NO}_2}^2 = k'_f c_{\text{NO}}^2 c_{\text{O}_2} - k_b c_{\text{NO}_2}^2$$

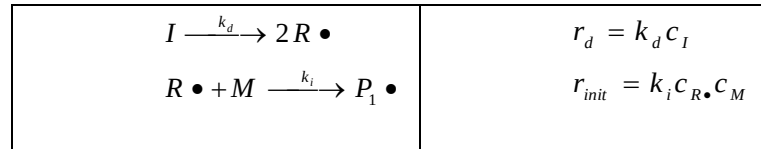
$$k'_f = k_{f,2} K_1 = A_{of,2} e^{-\frac{E_{f,2}}{RT}} e^{-\frac{\Delta_r G_1^\circ}{RT}} = A_{of,2} e^{\frac{\Delta_r S_1^\circ}{R}} e^{-\frac{(E_{f,2} + \Delta_r H_1^\circ)}{RT}} = A'_{of} e^{-\frac{E'_f}{RT}}$$

$$A'_{of} = A_{of,2} e^{\frac{\Delta_r S_1^\circ}{R}}, E'_f = E_{f,2} + \Delta_r H_1^\circ$$

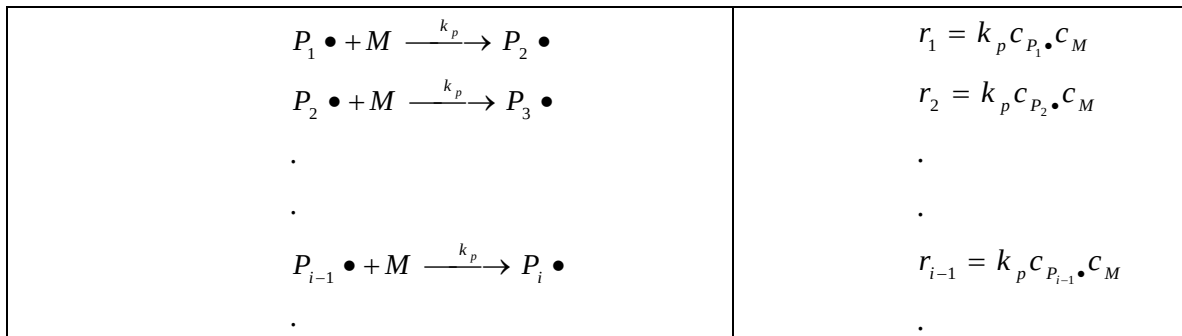


Radical polymerization

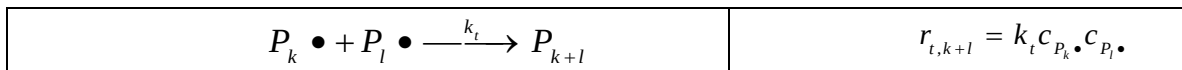
Initialization



Propagation



Termination



Intermediates

$$\frac{dc_{P_1\bullet}}{dt} = \frac{dc_{R\bullet}}{dt} = 0$$

Balance of initiator

$$2r_d - r_{init} = 0$$

$$2k_d c_I = k_i c_{R\bullet} c_M$$

$$c_{R\bullet} = \frac{2k_d c_I}{k_i c_M}$$

Balance of $P_1\bullet$

$$R_{P_1\bullet} = r_{init} - r_1 - r_{t,1} = k_i c_{R\bullet} c_M - k_p c_{P_1\bullet} c_M - k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

Balance of $P_k\bullet, k = 2, 3, \dots$

$$R_{P_k\bullet} = k_p c_{P_{k-1}\bullet} c_M - k_p c_{P_k\bullet} c_M - k_t c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

By summing the last equation from $k=2, 3, \dots$ and adding balance equation of $P_1\bullet$

$$k_i c_{R\bullet} c_M - k_t \left(\sum_{j=1}^{\infty} c_{P_j\bullet} \right)^2 = 0 \quad \longrightarrow \quad \sum_{j=1}^{\infty} c_{P_j\bullet} = \sqrt{\frac{k_i c_{R\bullet} c_M}{k_t}} = \sqrt{\frac{2k_d c_I}{k_t}}$$

Monomer consumption

$$R_M = -r_{init} - k_p c_M \sum_{j=1}^{\infty} c_{P_j \bullet} = - \left(k_i c_R \cdot c_M + k_p c_M \sum_{j=1}^{\infty} c_{P_j \bullet} \right) =$$

$$= - \left(2k_d c_I + k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M \right) \cong -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M$$

Polymer P_n production

$$R_{P_n} = \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}} \cdot c_{P_k \bullet}$$

Homework 5: to justify these equations

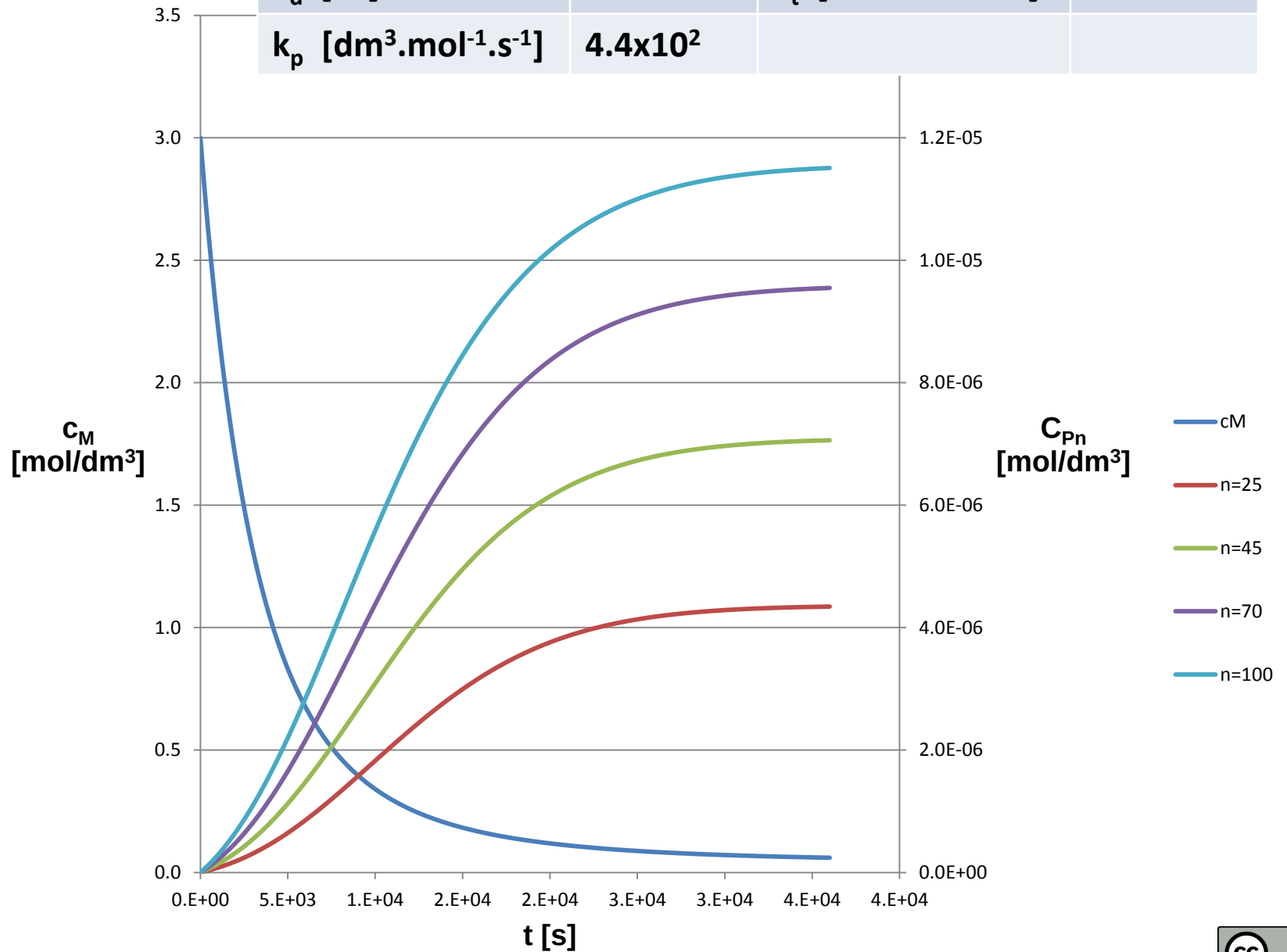


From balance of $P_k \bullet$

$$c_{P_k \bullet} = \frac{k_p c_{P_{k-1} \bullet} c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \longrightarrow c_{P_k \bullet} = \frac{k_p c_{P_{k-1} \bullet} c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} = \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \left[\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^{k-1}$$

$$R_{P_n} = \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}} \cdot c_{P_k \bullet} = \frac{(n-1)k_t}{2} \left[\frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^2 \left[\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right]^{n-2}$$

c_M^o [mol/dm ³]	3.0	c_I^o [mol/dm ³]	1.0×10^{-2}
k_d [s ⁻¹]	1.45×10^{-5}	k_t [dm ³ .mol ⁻¹ .s ⁻¹]	1.2×10^6
k_p [dm ³ .mol ⁻¹ .s ⁻¹]	4.4×10^2		



Summary

- Simple systems of elementary reactions
- Open x Closed sequence of elementary steps
- Quasi Steady State Hypothesis
- Practically important examples

4. The material balances for isothermal ideal reactor models



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Summary

- General material balance of reacting system
- Batch reactor
- Continuous-flow reactors: CSTR (Continuous Stirred Tank Reactor)
PFR (Plug Flow Reactor)
- Steady state of CSTR and PFR
- Design tasks : outlet (final conversion), given volume of reactor x volume of reactor, given outlet conversion

T=const.

Inlet convective molar flows (mol/s)

F_1^o

F_2^o

.

.

.

F_N^o

Arbitrary volume element

$$\sum_{i=1}^N \nu_{ki} A_i = 0 \quad k = 1, NR$$

$n_i(t)$

$V(t)$

Outlet convective molar flows (mol/s)

F_1

F_2

.

.

.

F_N

Molar balance of species i

$$F_i^o - F_i + \sum_{k=1}^{NR} \nu_{ki} \int_V r_{V,k} dV = \frac{\partial}{\partial t} \left(\int_V c_i dV \right) = \frac{\partial n_i}{\partial t}$$

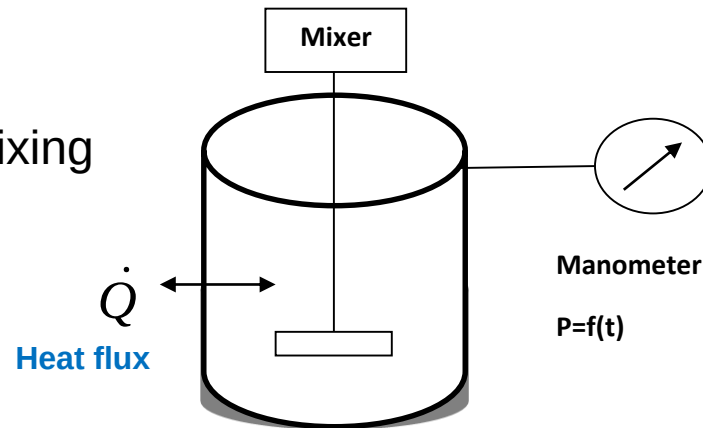
Overall molar balance

$$\sum_{i=1}^N [F_i^o - F_i] + \sum_{i=1}^N \sum_{k=1}^{NR} \nu_{ki} \int_V r_{V,k} dV = F^o - F + \sum_{k=1}^{NR} \Delta \nu_k \int_V r_{V,k} dV = \frac{\partial n}{\partial t}$$

$$\sum_{i=1}^N \nu_{ki} = \Delta \nu_k$$

Batch reactors

$V \neq \text{const.}$
 $T = \text{const.}$
 Perfect mixing



Laboratory
 Pharmaceutical industry
 Special chemicals
 Polymers

$$\sum_{i=1}^N \nu_{ki} A_i = 0 \quad k = 1, NR$$

$$n_i(t)$$

$V_R(t)$ – Volume of reaction mixture

Molar balance of species i

$$\cancel{F_i^0} - \cancel{F_i} + \sum_{k=1}^{NR} \nu_{ki} \int_{V_R} r_{V,k} dV = \frac{\partial n_i}{\partial t}$$

$$\frac{dn_i}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \cdot V_R$$

Reactor volume constant ($V_R = \text{const.}$)

$$\frac{1}{V_R} \frac{dn_i}{dt} = \frac{d\left(\frac{n_i}{V_R}\right)}{dt} = \frac{dc_i}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} (c_1, c_2, \dots, c_N)$$

Reactor pressure constant ($P = \text{const.}$)

$$n_i = c_i \cdot V_R$$

$$\frac{1}{V_R} \frac{dn_i}{dt} = \frac{1}{V_R} \frac{d(c_i \cdot V_R)}{dt} = \frac{dc_i}{dt} + c_i \frac{d \ln V_R}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k}$$

$$\frac{dc_i}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} - c_i \frac{d \ln V_R}{dt}$$

To calculate $P(t)$ or $V_R(t)$

state equation $f(T, P, V, \text{composition}) = 0$ is needed

Example

Constant volume isothermal batch reactor, ideal gas mixture

$$P = \frac{RT}{V_R} \sum_{j=1}^N n_j$$

$$\sum_{j=1}^N \nu_{kj} = \Delta \nu_k$$

$$\frac{dP}{dt} = \frac{RT}{V_R} \sum_{j=1}^N \frac{dn_j}{dt} = \frac{RT}{V_R} \sum_{j=1}^N V_R \sum_{k=1}^{NR} \nu_{kj} r_{V,k} = RT \sum_{k=1}^{NR} \Delta \nu_k r_{V,k}$$

Constant pressure isothermal batch reactor, ideal gas mixture

$$V_R = \frac{RT}{P} \sum_{j=1}^N n_j$$

$$\frac{dV_R}{dt} = \frac{RT}{P} \sum_{j=1}^N \frac{dn_j}{dt} = \frac{RT}{P} \sum_{j=1}^N V_R \sum_{k=1}^{NR} \nu_{kj} r_{V,k} = \frac{RTV_R}{P} \sum_{k=1}^{NR} \Delta \nu_k r_{V,k}$$

$$\frac{d \ln(V_R)}{dt} = \frac{RT}{P} \sum_{k=1}^{NR} \Delta \nu_k r_{V,k}$$

$$c_i = y_i \frac{P}{RT} \quad [*]$$

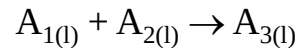
$$\frac{dc_i}{dt} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} - c_i \frac{RT}{P} \sum_{k=1}^{NR} \Delta \nu_k r_{V,k} =$$

$$= \sum_{k=1}^{NR} \nu_{ki} r_{V,k} - y_i \sum_{k=1}^{NR} \Delta \nu_k r_{V,k}$$

Example

Constant volume batch reactor, liquid mixture $\Rightarrow$ constant pressure

Second order irreversible reaction



$$r_V = kc_1c_2,$$

$$t = 0, c_1 = c_1^o, c_2 = c_2^o, c_3 = 0$$

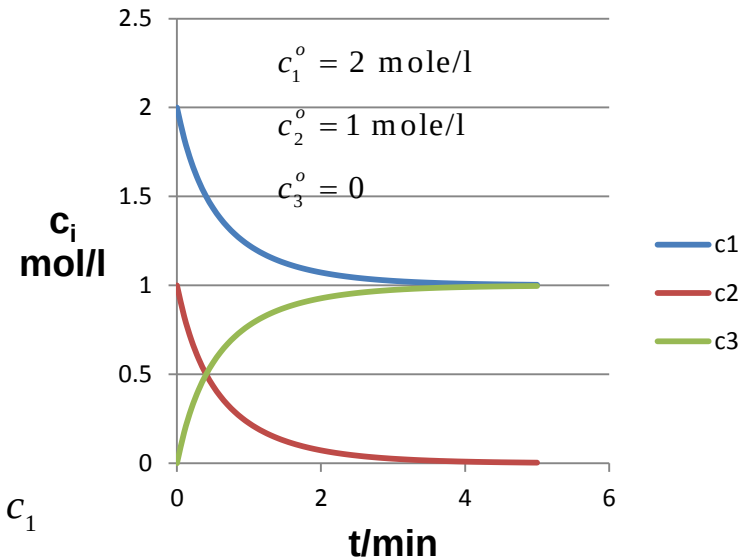
$$\frac{dc_i}{dt} = \nu_i r_V = \nu_i kc_1c_2$$

$$\frac{dc_1}{dt} = -kc_1c_2$$

$$\frac{dc_2}{dt} = -kc_1c_2$$

$$\frac{dc_3}{dt} = kc_1c_2$$

$$c_1 - c_1^o = c_2 - c_2^o, c_2 = c_1 - c_1^o + c_2^o, c_3 = c_1^o - c_1$$

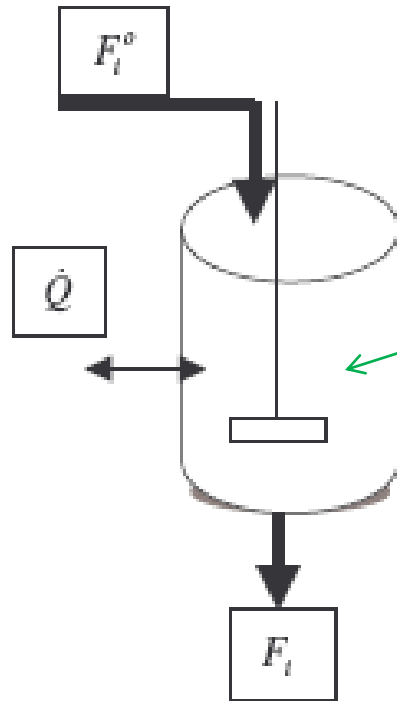


$$\frac{dc_1}{dt} = -kc_1(c_1 - c_1^o + c_2^o) \rightarrow \int_{c_1^o}^{c_1} \frac{dc_1}{c_1(c_1 - c_1^o + c_2^o)} = -k \int_0^t dt \rightarrow c_1 = \frac{(c_1^o - c_2^o)}{1 - \frac{c_2^o}{c_1^o} e^{(c_2^o - c_1^o)kt}}$$

$$c_1^o = c_2^o \quad c_1 = \left(\frac{1}{c_1^o} + kt \right)^{-1}$$

Continuous-flow reactors

Continuous Stirred Tank Reactor – CSTR



$$\sum_{i=1}^N \nu_{ki} A_i = 0 \quad k = 1, NR$$

$$n_i(t)$$

$$V_R = \text{const} - \text{Volume of reactor}$$

Molar balance of species i

$$F_i^0 - F_i + \sum_{k=1}^{NR} \nu_{ki} r_{V,k} V_R = \frac{dn_i}{dt}$$

Overall molar balance

$$F^0 - F + \sum_{k=1}^{NR} \Delta \nu_k r_{V,k} V_R = \frac{dn}{dt}$$

We need supplementary information

- state behavior of reaction mixture
- start-up (shut-down) molar flow rates of individual species

Constant pressure isothermal CSTR, ideal gas mixture

$$RT \sum_{j=1}^N n_j = pV_R$$

It arises from overall molar balance (volume of reactor, V_R is constant)

$$\frac{d \sum_{j=1}^N n_j}{dt} = \sum_{i=1}^N \frac{dn_i}{dt} = F^o - F + V_R \sum_{i=1}^N \sum_{k=1}^{NR} \nu_{ki} r_{V,k} = F^o - F + V_R \sum_{k=1}^{NR} \Delta \nu_k r_{V,k} = 0$$

$$F = F^o + V_R \sum_{k=1}^{NR} \Delta \nu_k r_{V,k}$$

and molar balance of species i becomes

$$\frac{dn_i}{dt} = F_i^o - y_i \left(F^o + V_R \sum_{k=1}^{NR} \Delta \nu_k r_{V,k} \right) + V_R \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \quad F_i^o = y_i^o F^o$$

$$\frac{dn_i}{dt} = \frac{PV_R}{RT} \frac{dy_i}{dt} = F^o (y_i^o - y_i) + V_R \left(\sum_{k=1}^{NR} (\nu_{ki} - y_i \Delta \nu_k) r_{V,k} \right)$$

$$\frac{dy_i}{dt} = \frac{RTF^o}{PV_R} (y_i^o - y_i) + \frac{RT}{P} \left(\sum_{k=1}^{NR} (\nu_{ki} - y_i \Delta \nu_k) r_{V,k} \right) \quad i = 1, N$$

Inlet volumetric flow rate is

$$\frac{RTF^o}{P} = \dot{V}_o$$

Mean residence time of reaction mixture (based on inlet flow rate) is given by

$$\bar{\tau}_o = \frac{V_R}{\dot{V}_o} = \frac{PV_R}{RTF^o}$$

and molar balance of species i becomes finally

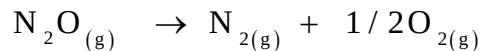
$$\frac{dy_i}{dt} = \frac{1}{\bar{\tau}_o} (y_i^o - y_i) + \frac{RT}{P} \left(\sum_{k=1}^{NR} (\nu_{ki} - y_i \Delta \nu_k) r_{V,k} \right) \quad i = 1, N$$

If only one reaction takes place:

$$\frac{dy_i}{dt} = \frac{1}{\bar{\tau}_o} (y_i^o - y_i) + \frac{RT}{P} (\nu_i - y_i \Delta \nu) r_V \quad i = 1, N$$

Example

Start-up of an isothermal CSTR



$$V_R = 0.1 \text{ l} = 10^{-4} \text{ m}^3, T = 320^\circ \text{C}, P = 101 \text{ kPa}$$

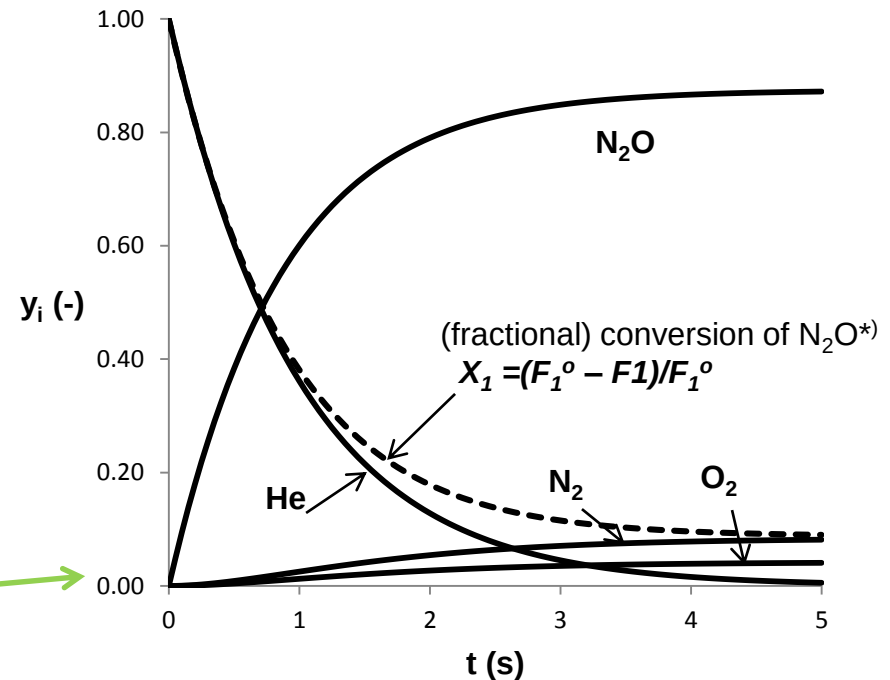
$$r_V = k P_{\text{N}_2\text{O}}, k = 2.028 \times 10^{-5} \text{ mole} \cdot \text{Pa}^{-1} \cdot \text{min}^{-1} \cdot \text{m}^{-3}$$

$$y_1^o = 1, y_2^o = y_3^o = y_4^o = 0 \quad (1 = \text{N}_2\text{O}, 2 = \text{O}_2, 3 = \text{N}_2, 4 = \text{He})$$

$$t = 0, y_1 = 0 = y_2 = y_3 = 0, y_4 = 1$$

$$\bar{\tau}_o = 1$$

Numerical solution of balance equations



*) The equation is valid only at steady state

Steady state

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

If only one reaction takes place:

$$F_i - F_i^o = V_R \nu_i r_V, \quad i = 1, N$$

using fractional conversion of key species j

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

$$F_j^o X_j = V_R |\nu_j| r_V(X_j)$$

a) The volume of reactor for given outlet conversion

$$V_R = F_j^o \frac{X_j}{|\nu_j| r_V(X_j)}$$

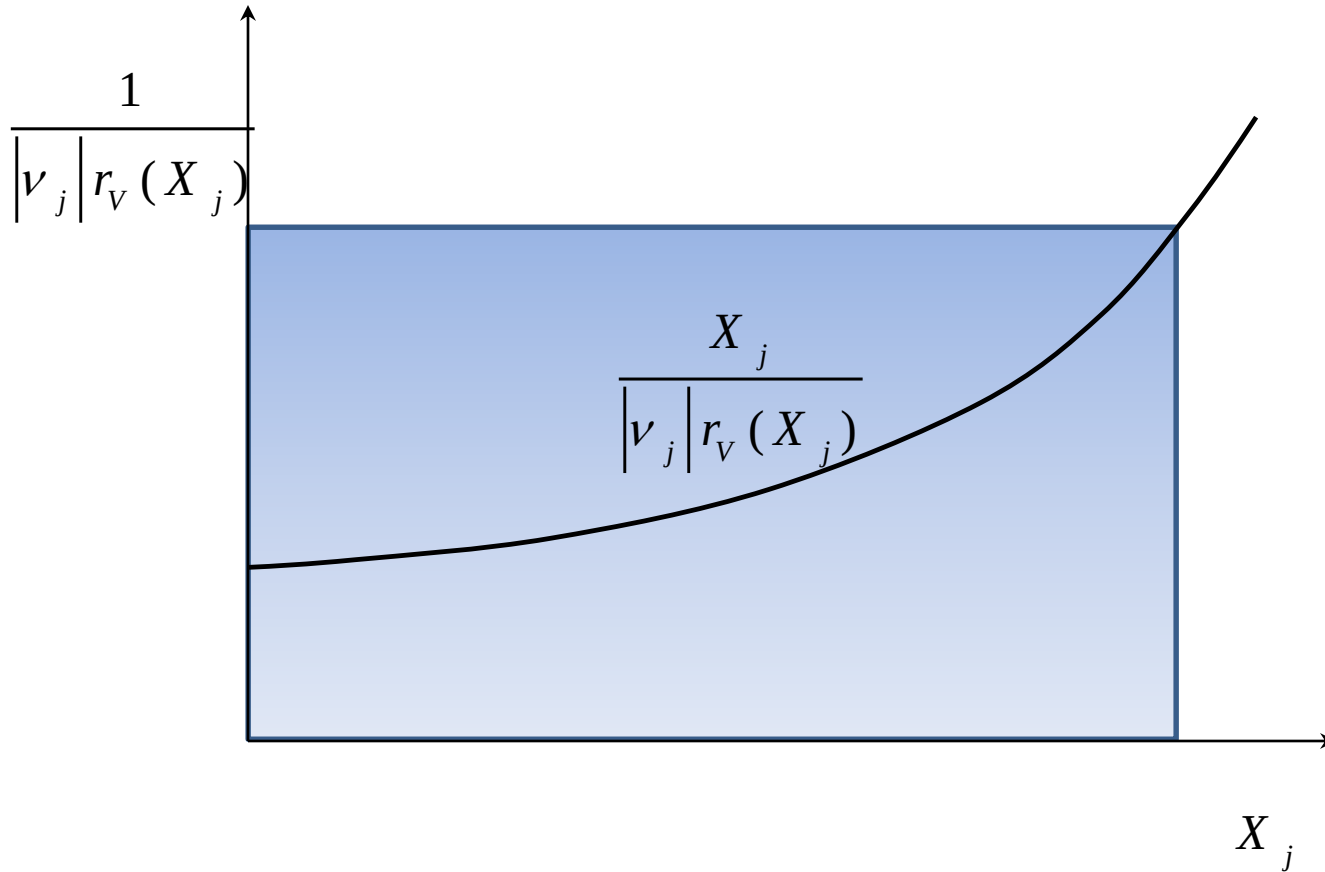
Simple substitution

b) The outlet conversion for given volume of reactor

$$\frac{F_j^o}{V_R} X_j - |\nu_j| r_V(X_j) = f(X_j) = 0$$

Graphical or numerical (iterative)
solution

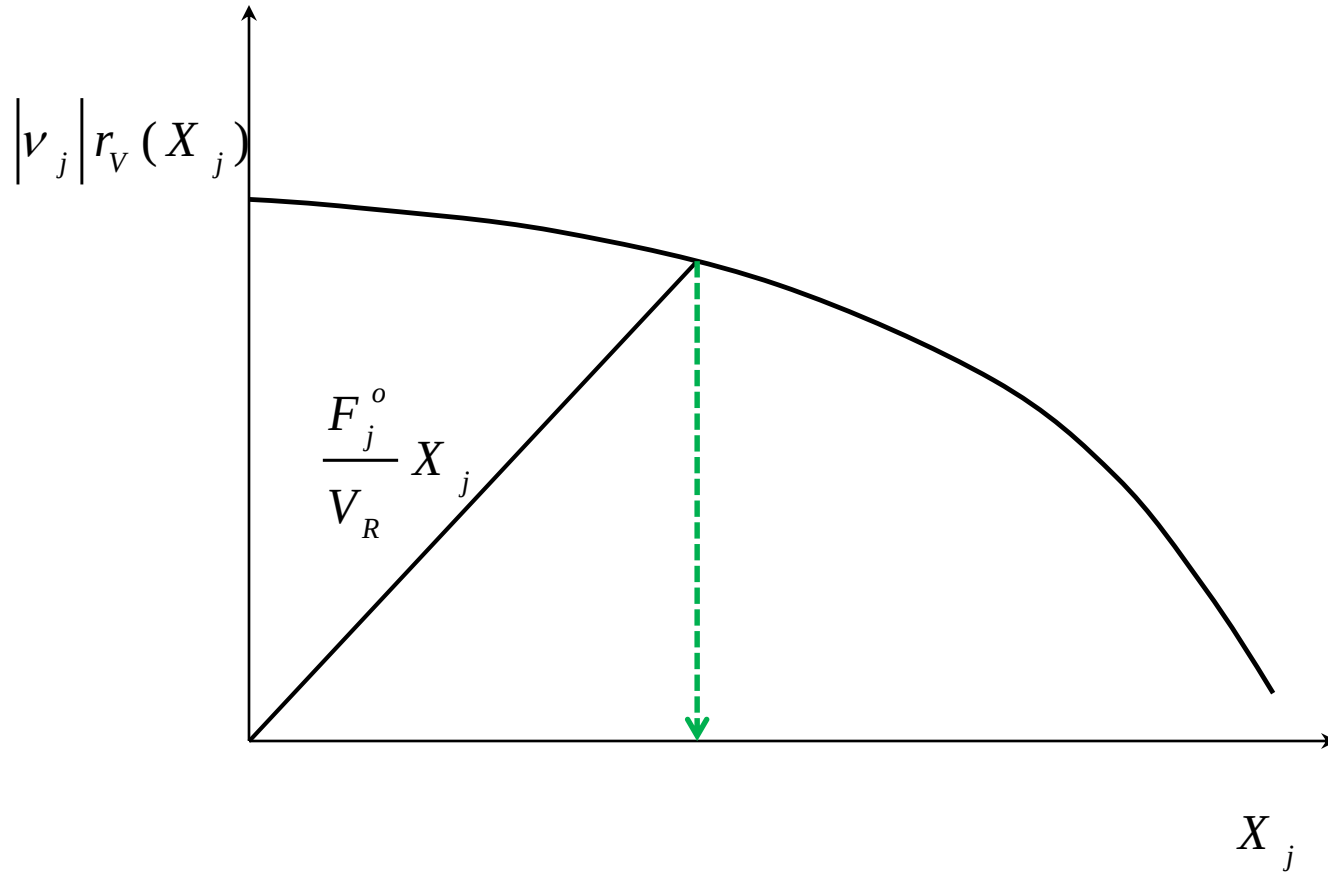
Graphical assessment of the CSTR volume



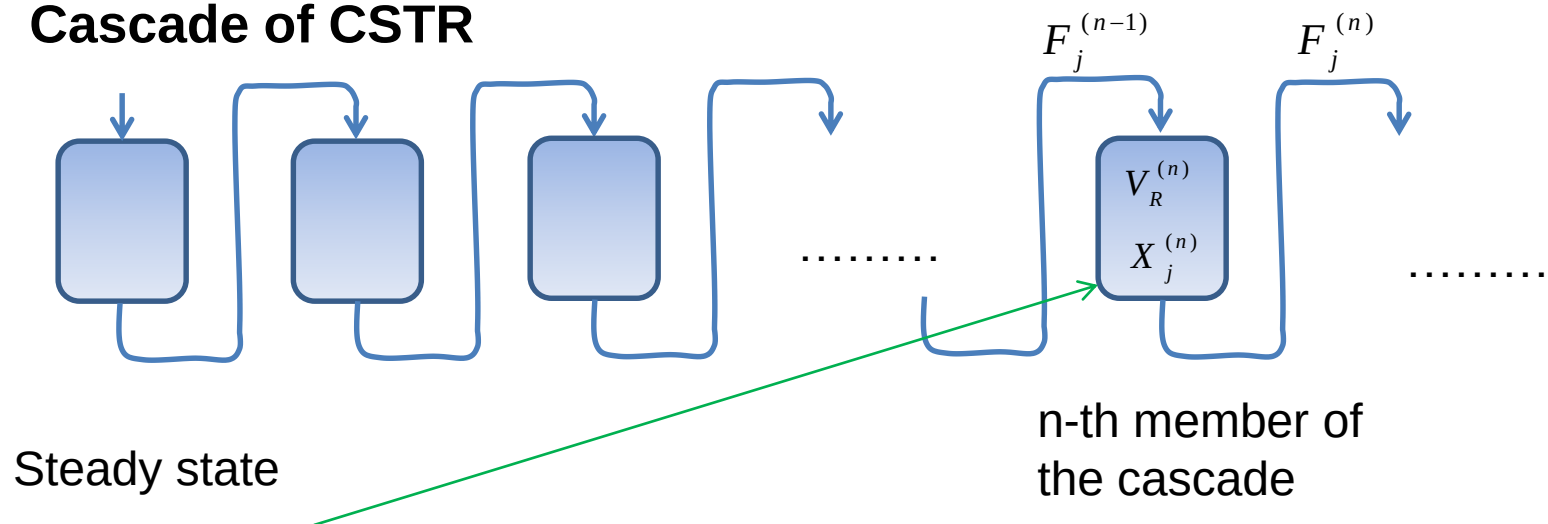
Levenspiel
diagram

usually $|v_j| = 1$

Graphical assessment of the outlet conversion



Cascade of CSTR



$$F_i^{(n)} - F_i^{(n-1)} = V_R^{(n)} \nu_i r_V^{(n)}, \quad i = 1, N \quad n = 1, N_{CSTR}$$

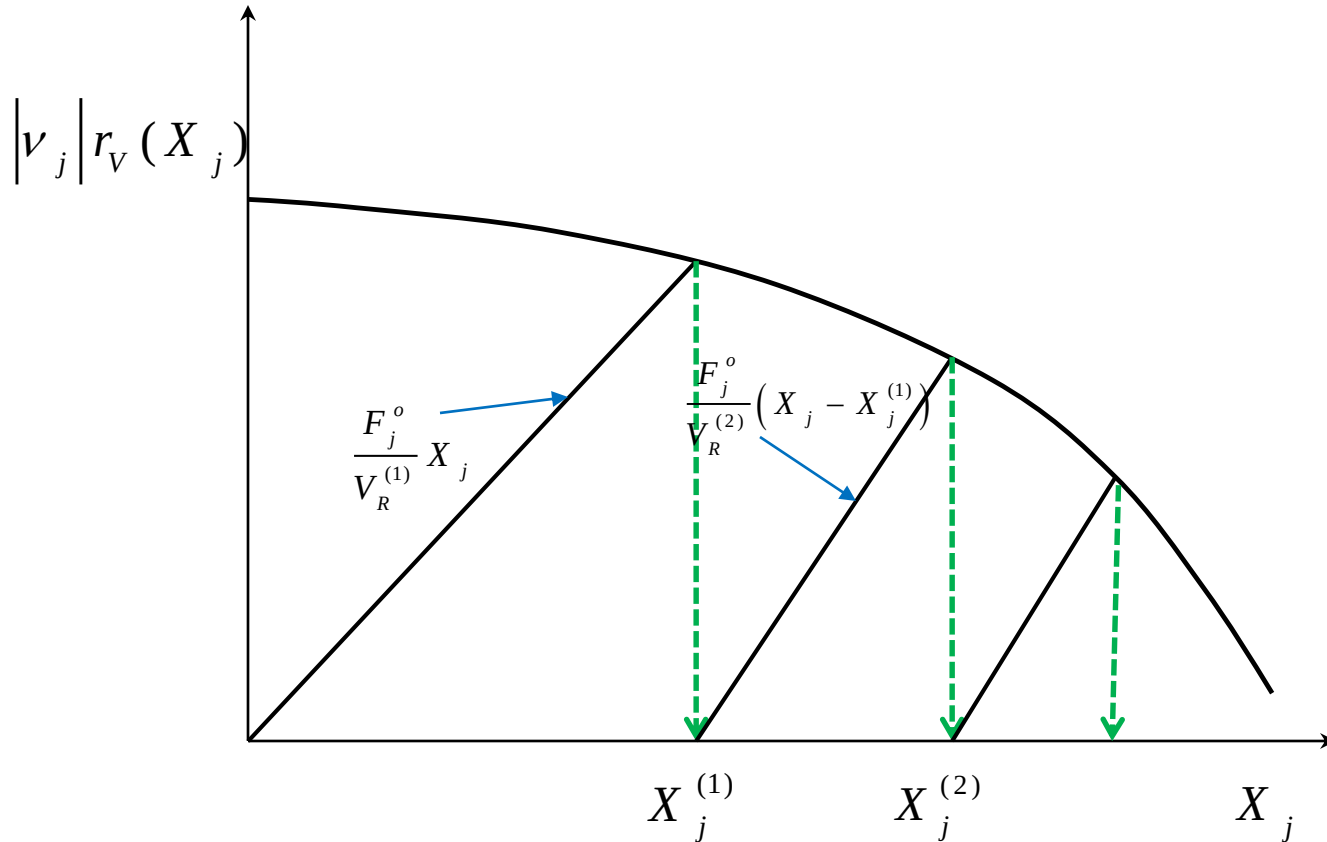
$$X_j^{(n)} = \frac{F_j^o - F_j^{(n)}}{F_j^o}$$

$$F_j^{(n)} = F_j^o (1 - X_j^{(n)})$$

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

$$\frac{F_j^o}{V_R^{(n)}} (X_j^{(n)} - X_j^{(n-1)}) = |\nu_j| r_V(X_j^{(n)}), \quad n = 1, N_{CSTR}$$

Graphical assessment of the outlet conversion in the cascade of CSTR

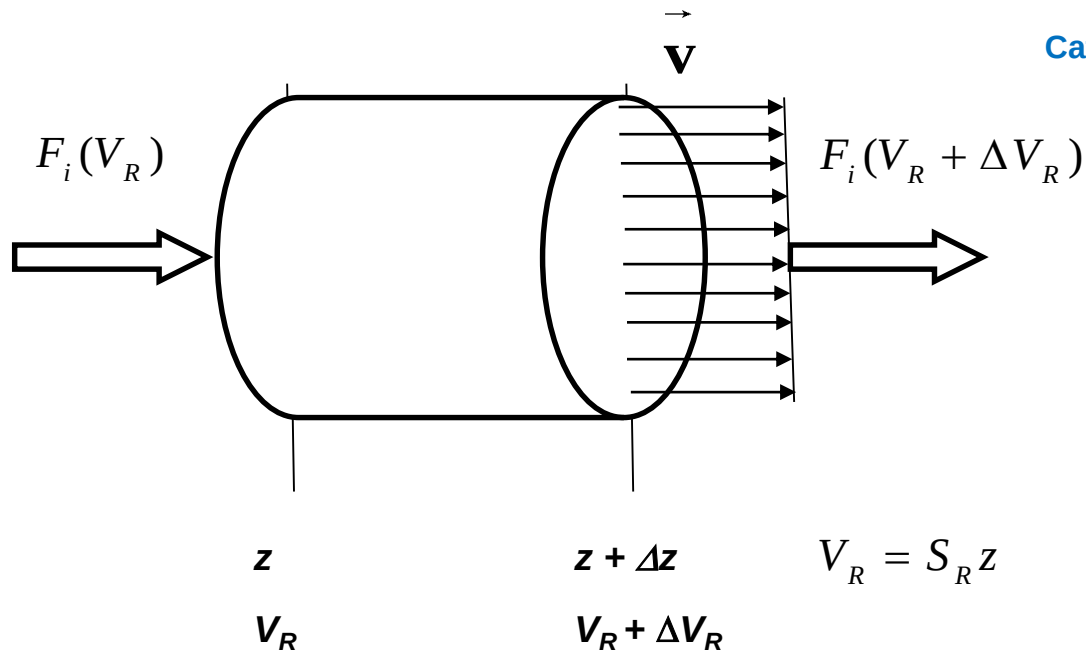


Homework 6

Prove that $X_j^{(n)} = 1 - (1 + k\bar{\tau}_o)^{-n}$, $\bar{\tau}_o = \frac{V_R^{(n)}}{\dot{V}_o}$ for first order constant-volume reaction.

In the limit $\lim_{n \rightarrow \infty} X_j^{(n)} = 1 - e^{-k\bar{\tau}_{oR}}$, $\bar{\tau}_{oR} = \frac{nV_R^{(n)}}{\dot{V}_o}$

Plug Flow reactor – PFR



Tubular reactors
 High production capacity
 Catalytic reactors (e.g. ammonia synthesis)

Molar balance of species i

$$\frac{\partial c_i(t, z)}{\partial t} = -\frac{1}{S_R} \frac{\partial F_i(t, z)}{\partial z} + \sum_{k=1}^{NR} \nu_{ki} r_{V,k}(t, z) \quad i = 1, N$$

Steady state

$$\frac{dF_i}{dV_R} = \sum_{k=1}^{NR} \nu_{ki} r_{V,k} \quad i = 1, N$$

If only one reaction takes place:

$$\frac{dF_i}{dV_R} = \nu_i r_V \quad i = 1, N$$

using fractional conversion of key species j

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

$$F_j^o \frac{dX_j}{dV_R} = |\nu_j| r_V(X_j)$$

useful relations:

$$F_j^o \int_{X_j(1)}^{X_j(2)} \frac{dX_j}{|\nu_j| r_V(X_j)} = V_R$$

$$y_i = \frac{F_i}{\sum_{j=1}^N F_j}, c_i = \frac{F_i}{V_m \sum_{j=1}^N F_j} = \frac{y_i}{V_m} = \frac{F_i}{V}$$

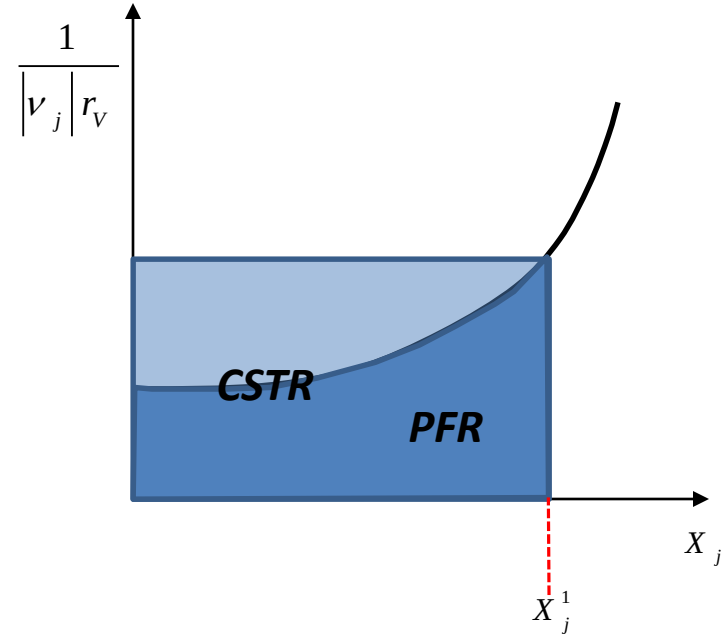
V_m – molar volume ($\text{m}^3 \text{mole}^{-1}$)

BATCH, CSTR, PFR (PBCR), one reaction, fractional conversion of key component

BATCH

$$-\frac{n_j^o}{\nu_j V_R} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)} = \int_0^{t_R} dt = t_R$$

$$\frac{c_j^o}{|\nu_j|} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)} = \int_0^{t_R} dt = t_R$$



CSTR

$$V_R = -\frac{F_j^o}{\nu_j} \frac{X_j^1}{r_V(X_j^1)} = \frac{F_j^o}{|\nu_j|} \frac{X_j^1}{r_V(X_j^1)}$$

PBCR

Packed Bed Catalytic Reactor

PFR

$$V_R = -\frac{F_j^o}{\nu_j} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)} = \frac{F_j^o}{|\nu_j|} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)}$$

$$W = -\frac{F_j^o}{\nu_j} \int_0^{X_j^1} \frac{dX_j}{r_M} = \frac{F_j^o}{|\nu_j|} \int_0^{X_j^1} \frac{dX_j}{r_M(X_j)}$$

Mean residence time

$$\bar{\tau} = \frac{V_R}{\dot{V}}$$

BATCH, PFR

$$\frac{c_j^o}{|\nu_j|} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)} = \bar{\tau}_o$$

CSTR

$$\frac{c_j^o}{|\nu_j|} \frac{X_j^1}{r_V(X_j^1)} = \bar{\tau}_o$$

$$\bar{\tau}_o = \frac{V_R}{\dot{V}_o}$$

$\dot{V}_o$ volumetric flow rate (m³/s) of reaction mixture at inlet conditions

Gas Hourly Space Velocity

$$GHSV = \frac{\text{Gas volumetric flow rate (m}^3\text{/hr)}}{\text{Volume of reactor (m}^3\text{)}}$$

Liquid Hourly Space Velocity

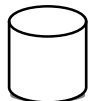
$$LHSV = \frac{\text{Liquid volumetric flow rate (m}^3\text{/hr)}}{\text{Volume of reactor (m}^3\text{)}}$$

Tasks

- 1. Calculate the volume of reactor (mass of catalyst) (CSTR, PFR, PBCR) or time of reaction (BATCH) to obtain given conversion.***
- 2. Calculate the outlet conversion for given volume of reactor.***
- 3. Calculate the reaction rate in laboratory reactor to obtain kinetic law and estimate the kinetic parameters.***

$$NR = 1 \quad \sum_{i=1}^N \nu_i A_i = 0 \quad \Delta \nu = \sum_{i=1}^N \nu_i \quad j - \text{subscript of key component}$$

BATCH



FLOW



$$n_i = n_i^o + \nu_i \xi = n_i^o - \frac{\nu_i}{\nu_j} n_j^o \cdot X_j$$

$$F_i = F_i^o + \nu_i \int r_V \cdot dV_R = F_i^o - \frac{\nu_i}{\nu_j} F_j^o \cdot X_j$$

$$n = \sum_{i=1}^N n_i^o + \xi \sum_{i=1}^N \nu_i = n^o + \xi \cdot \Delta \nu = n^o - \frac{\Delta \nu}{\nu_j} n_j^o \cdot X_j$$

$$F = F^o - \frac{\Delta \nu}{\nu_j} F_j^o \cdot X_j$$

$$x_i = \frac{n_i}{n} = \frac{n_i^o - \frac{\nu_i}{\nu_j} n_j^o \cdot X_j}{n^o - \frac{\Delta \nu}{\nu_j} n_j^o \cdot X_j} = \frac{x_i^o - \frac{\nu_i}{\nu_j} x_j^o \cdot X_j}{1 - \frac{\Delta \nu}{\nu_j} x_j^o \cdot X_j}$$

$$x_i = \frac{F_i}{F} = \frac{F_i^o - \frac{\nu_i}{\nu_j} F_j^o \cdot X_j}{F^o - \frac{\Delta \nu}{\nu_j} F_j^o \cdot X_j} = \frac{x_i^o - \frac{\nu_i}{\nu_j} x_j^o \cdot X_j}{1 - \frac{\Delta \nu}{\nu_j} x_j^o \cdot X_j}$$

$$c_i = \frac{n_i}{V} = \frac{n_i}{n \cdot V_m} = \frac{x_i}{V_m} = \frac{1}{V_m} \frac{x_i^o - \frac{\nu_i}{\nu_j} x_j^o \cdot X_j}{1 - \frac{\Delta \nu}{\nu_j} x_j^o \cdot X_j}$$

$$c_i = \frac{F_i}{\dot{V}} = \frac{F_i}{F \cdot V_m} = \frac{x_i}{V_m} = \frac{1}{V_m} \frac{x_i^o - \frac{\nu_i}{\nu_j} x_j^o \cdot X_j}{1 - \frac{\Delta \nu}{\nu_j} x_j^o \cdot X_j}$$

V_m - molar volume of reaction mixture
(m³/mol)

Gas phase - Ideal state behavior

$$V_m = \frac{RT}{P}$$

$$c_i = \frac{\frac{x_i}{RT}}{\frac{P}{RT}} = \frac{P_i}{RT} = \frac{P}{RT} \frac{x_i^o - \frac{v_i}{v_j} x_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o \cdot X_j}$$

$$c_i = \frac{\frac{F_i}{V}}{\frac{F}{P} \cdot \frac{RT}{P}} = \frac{P_i}{RT} = \frac{P}{RT} \frac{x_i^o - \frac{v_i}{v_j} x_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o \cdot X_j}$$

$$c_i = \frac{n_i}{V} = \frac{n_i}{V_o \frac{T}{T_o} \frac{P_o}{P} (1 - \frac{\Delta v}{v_j} x_j^o X_j)} =$$

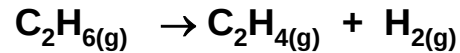
$$= \frac{T_o}{T} \frac{P}{P_o} \frac{1}{V_o} \left(\frac{n_i^o - \frac{v_i}{v_j} n_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o X_j} \right) = \frac{T_o}{T} \frac{P}{P_o} \left(\frac{c_i^o - \frac{v_i}{v_j} c_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o X_j} \right)$$

$$c_i = \frac{\frac{F_i}{V}}{\dot{V}_o \frac{T}{T_o} \frac{P_o}{P} \left(1 - \frac{\Delta v}{v_j} x_j^o X_j \right)} =$$

$$= \frac{T_o}{T} \frac{P}{P_o} \frac{1}{\dot{V}_o} \left(\frac{F_i^o - \frac{v_i}{v_j} F_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o X_j} \right) = \frac{T_o}{T} \frac{P}{P_o} \left(\frac{c_i^o - \frac{v_i}{v_j} c_j^o \cdot X_j}{1 - \frac{\Delta v}{v_j} x_j^o X_j} \right)$$

Homework 7

Calculate volume of PFR to produce 150 kt ethylen/year. Reaction of the 1st order



takes place at 1100 K and 0,6 Mpa. Final conversion of ethan is 80 %. Reaction rate is given by

$$r_V = k \cdot c_A$$

$$k (1000 \text{ K}) = 0,072 \text{ s}^{-1} \quad E = 343,6 \text{ kJ/mol}$$

Pure ethan is fed into the reactor.

Assumptions:

Ideal gas, molar weight of ethylen is 28,054 kg/kmol.

K. J. Laidler and B. W. Wojciechowski: Kinetics and Mechanisms of the Thermal Decomposition of Ethane.
I. The Uninhibited Reaction, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 260, No. 1300 pp. 91-102

Homework 4 (due after Chapter 4)

Calculate volumes of CSTR a PFR working at 150 °C and 300 kPa to produce 1 t COCl₂/day with CO conversion equal to 95 %. A mixture of CO and Cl₂ (molar ratio 1:1) is fed at 300 kPa and 150 °C.

Data

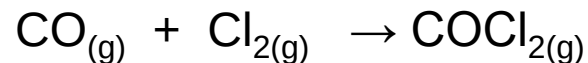
$$k(423 \text{ K}) = 0.07 \text{ (m}^3\text{mol}^{-1})^{3/2}\cdot\text{s}^{-1}$$

$$M_{\text{COCl}_2} = 98.92 \text{ kg/kmol.}$$

Answer:

$$V_{\text{CSTR}} = 0.053 \text{ m}^3$$

$$V_{\text{PFR}} = 0.0021 \text{ m}^3$$



$$F_i^o \rightarrow \boxed{} \rightarrow F_i \quad F_i = F_i^o - \frac{v_i}{v_j} F_j^o X_j$$

steady state; j - key component

	IN	OUT
CO (1)	F_1^o	$F_1 = F_1^o (1 - X_1)$
Cl ₂ (2)	F_1^o	$F_2 = F_1^o (1 - X_1)$
COCl ₂ (3)	0	$F_3 = F_1^o X_1$
Σ	$F^o = 2 F_1^o$	$F = F_1^o (2 - X_1)$

$$\text{ideal gas} \Rightarrow V_m = \frac{RT}{P} \quad [\text{m}^3/\text{mol}]$$

$$c_{CO} = c_1 = \frac{F_1}{V} = \frac{F_1}{V_m F} = \frac{P}{RT} \frac{F_1}{F} = \frac{P}{RT} \frac{F_1^o (1 - X_1)}{F_1^o (2 - X_1)} = \frac{P}{RT} \frac{(1 - X_1)}{(2 - X_1)} = c_{Cl_2} = c_2 \quad [\text{mol}/\text{m}^3]$$

$$r_V = k c_{CO} c_{Cl_2}^{3/2} = k \left(\frac{P}{RT} \right)^{5/2} \left(\frac{1 - X_1}{2 - X_1} \right)^{5/2} \quad [\text{mol}/\text{m}^3/\text{s}]$$

$$F_1^o = \frac{F_3}{X_1^1} = \frac{1 \times 10^6 / 98.92 / (24 \times 3600)}{0.95} = 0.123163 \text{ mol/s}$$

$$V_{CSTR} = \frac{F_1^o}{|\nu_1|} \frac{X_1^1}{r_V(X_1^1)} = \frac{F_1^o}{|-1|} \frac{X_1^1}{k \left(\frac{P}{RT} \right)^{5/2} \left(\frac{1 - X_1^1}{2 - X_1^1} \right)^{5/2}} = \frac{0.123163 \times 0.95}{0.07 \times \left(\frac{300 \times 10^3}{8.3145 \times 423} \right)^{5/2} \left(\frac{1 - 0.95}{2 - 0.95} \right)^{5/2}} =$$

$$= 0.0503 \text{ m}^3$$

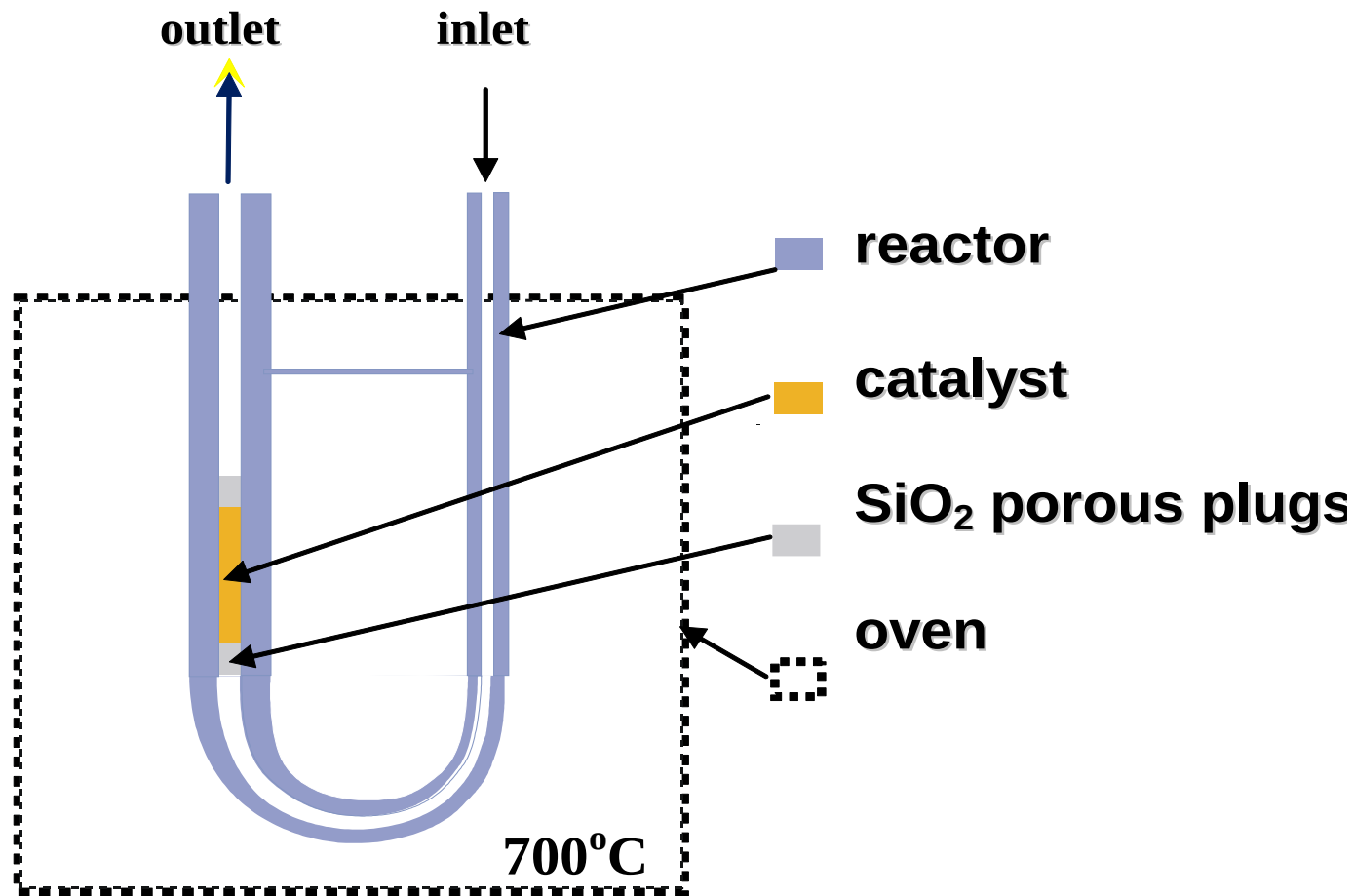
$$\begin{aligned}
 V_{PFR} &= \frac{F_j^o}{|v_j|} \int_0^{X_j^1} \frac{dX_j}{r_V(X_j)} = \frac{F_1^o}{|-1|} \int_0^{0.95} \frac{dX_1}{k \left(\frac{P}{RT} \right)^{5/2} \left(\frac{1-X_1}{2-X_1} \right)^{5/2}} = \frac{F_1^o}{k} \left(\frac{RT}{P} \right)^{5/2} \int_0^{0.95} \left(\frac{2-X_1}{1-X_1} \right)^{5/2} dX_1 = \\
 &= \frac{0.123163}{0.07} \times \left(\frac{8.3145 \times 423}{300 \times 10^3} \right)^{5/2} \times 79.42692225 = 2.08 \times 10^{-3} \text{ m}^3
 \end{aligned}$$

Summary

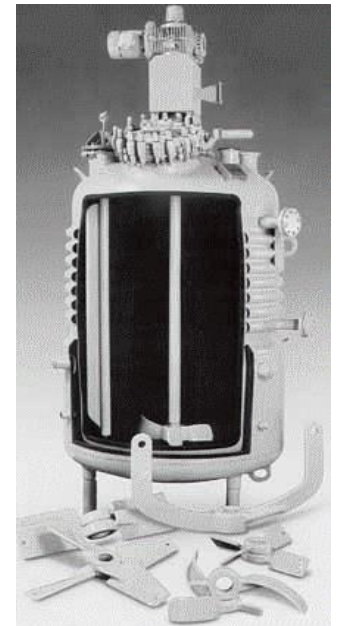
- General material balance of reacting system
- Batch reactor
- Continuous-flow reactors: CSTR (Continuous Stirred Tank Reactor)
PFR (Plug Flow Reactor)
- Steady state of CSTR and PFR
- Design tasks : outlet (final conversion), given volume of reactor x volume of reactor, given outlet conversion

5. Kinetic parameters estimation from isothermal experimental data

Flow catalytic reactor



Batch high pressure reactor



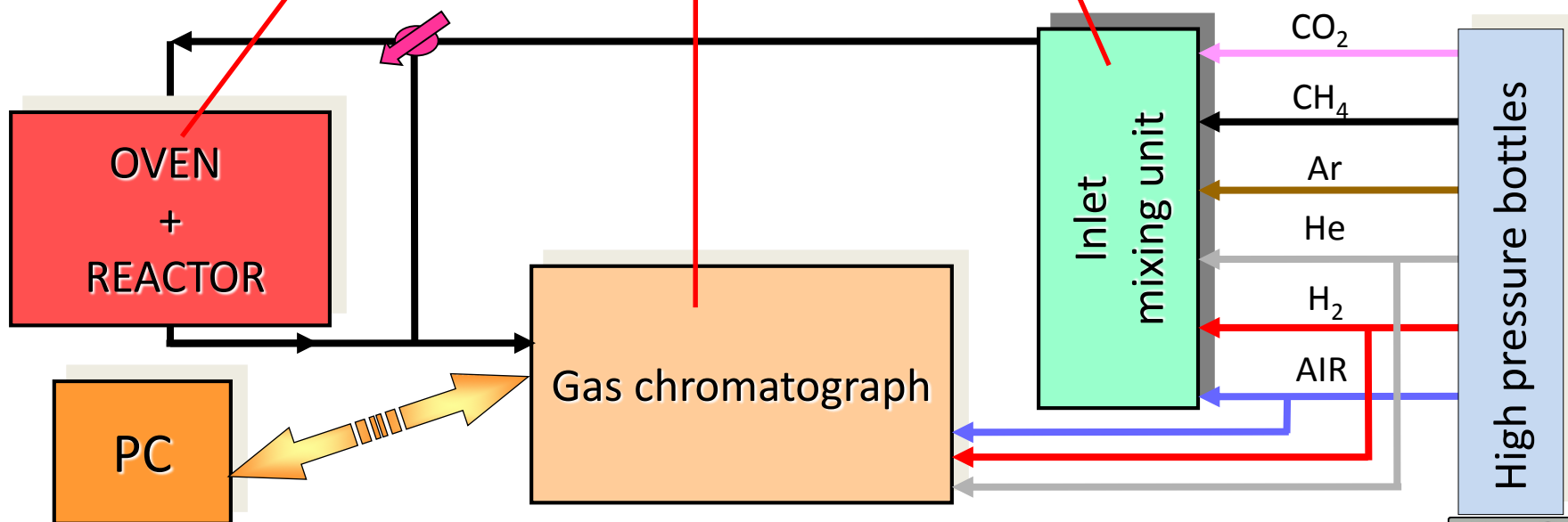
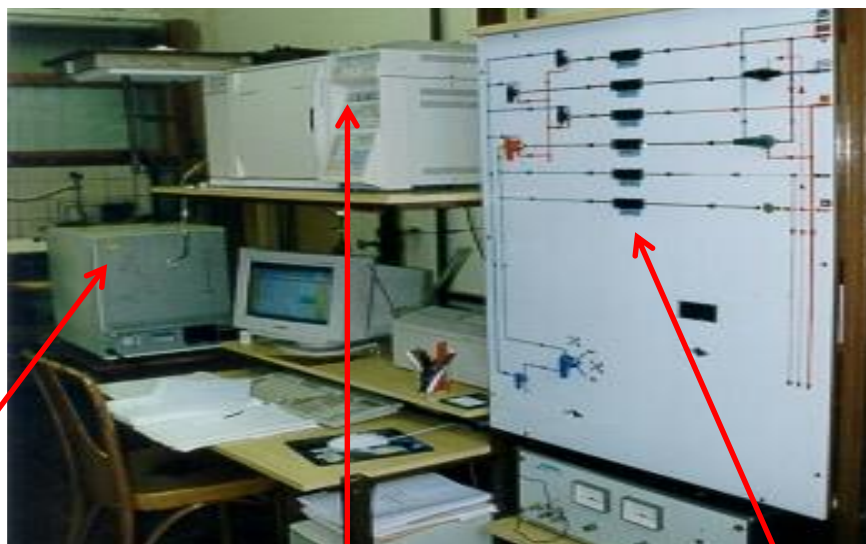
EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education



MINISTRY OF EDUCATION,
YOUTH AND SPORTS



Laboratory flow reactor for kinetic experiments



Reaction rate evaluation from ideal reactors

CSTR

- + Direct calculation of r.r.
- Temperature control
- Ideal mixing

$$r_V = \frac{F_j^o X_j}{|\nu_j| V_R}$$

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

PFR

- + Simple realization
- + High range of V_R/F
- Gradients of temperature and composition

$$r_V = \frac{1}{|\nu_j|} \frac{dX_j}{d(V_R / F_j^o)}$$

BATCH

- + Simple realization
- Temperature control
- Ideal mixing

$$r_V = \frac{1}{|\nu_j|} \frac{n_j^o}{V_R} \frac{dX_j}{dt}$$

Strategy of kinetic experiment

1. Choice of measured components
2. Choice of reactor
3. Formulation of kinetic model based on mechanism of reaction and mathematical model of reactor $r = f_1(T) \cdot f_2(c_i) \cdot f(\text{catalyst activity}) \dots$
4. Choice of temperature, composition and flow rate range
5. Statistical method for kinetic parameter estimation
6. Experimental data measurement
7. Evaluation of kinetic parameters
8. Results analysis  Does the kinetic model describe *well* our data ?

NO



YES



END

Experimental methods

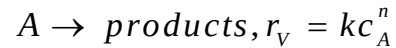
Methods “Ex-situ” and “In-situ”

- > gas chromatography, mass spectrometry, UV-VIS spectrometry ...
- > NMR, FTIR, electrochemical methods...
- > volume variation, optical properties, temperature variation, mass variation, ...

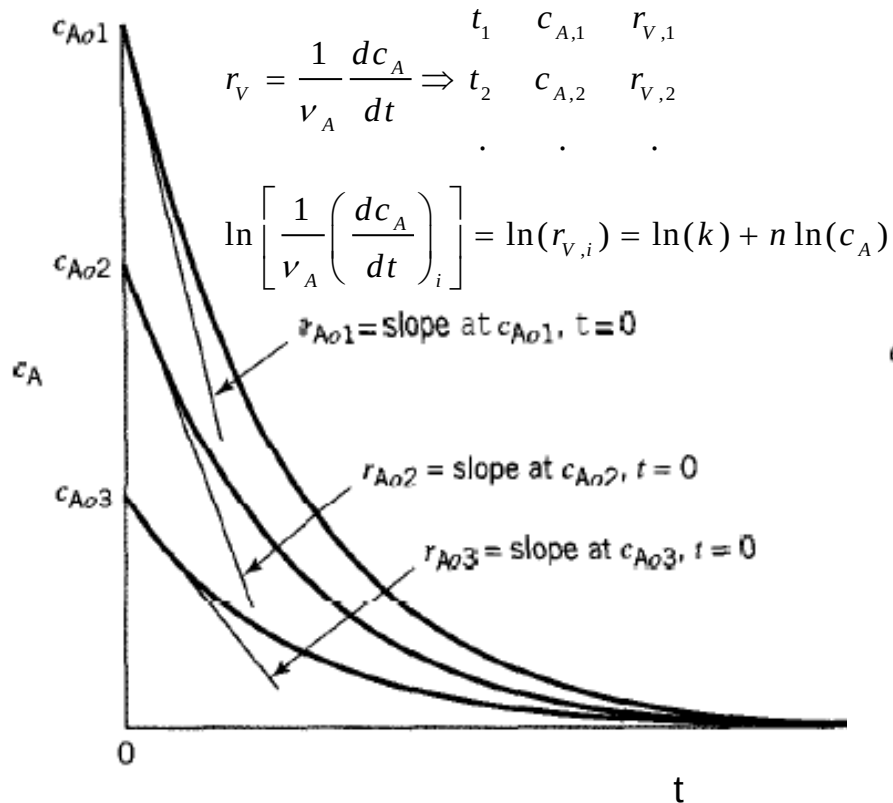
Kinetic parameters estimation

Isothermal batch reactor, constant volume

Example:

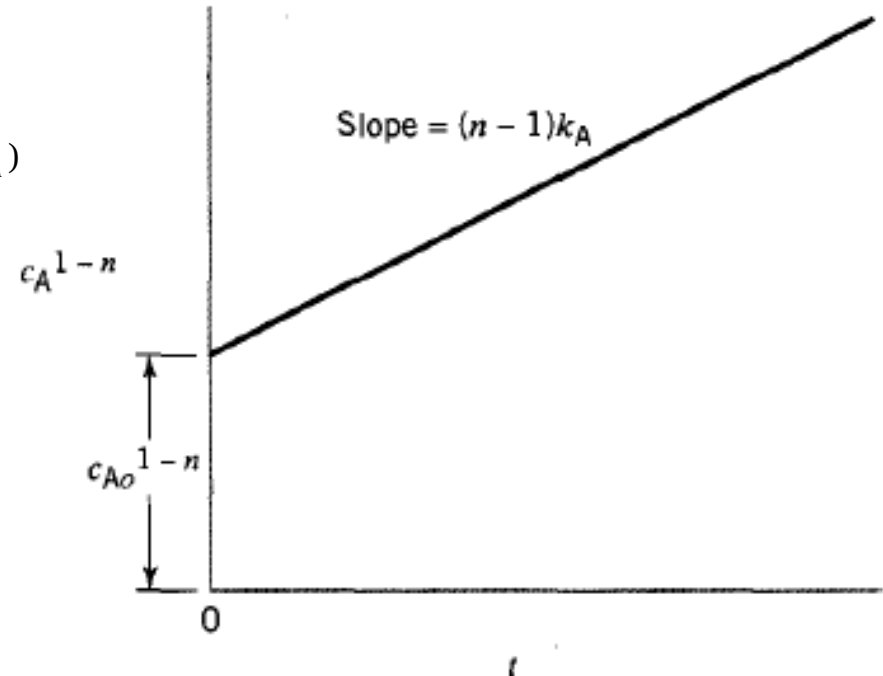


Differential method



Integral method

$$c_A^{1-n} = (c_A^o)^{1-n} + (n-1)kt \quad (n \neq 1), \quad c_A = c_A^o e^{-kt} \quad (n = 1)$$



Example

Diazobenzenchloride is decomposed following stoichiometric equation:



1 l of solution containing 150 g $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ was placed in an isothermal batch reactor. The volume of evolving nitrogen was measured as a function of time at 70°C and at 100 kPa:

t [min]	0	1	2	3	4	5	6	7
volume N ₂ [litr]	0	1.66	3.15	4.49	5.71	6.81	7.82	8.74

We should

- formulate a mathematical model of reactor,
- determine a reaction rate at given interval of time by the differential method,
- estimate a reaction rate constant and order of reaction with respect to $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ using differential method,
- estimate a reaction rate constant and order of reaction with respect to $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ using integral method.

We assume ideal gas, constant volume of liquid phase, negligible solubility of nitrogen in liquid phase.

Molar weight of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ is 140,572 kmol/kg.

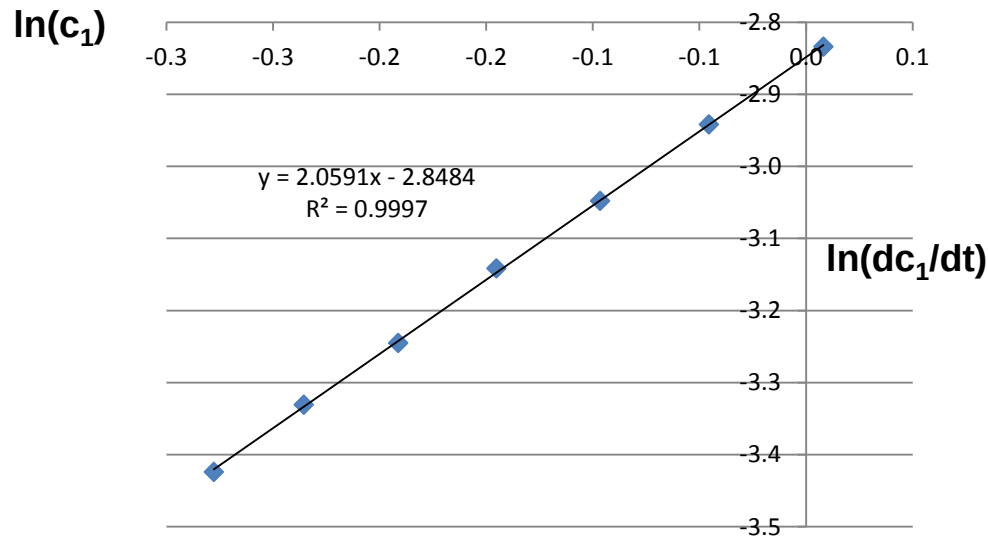
Differential method

t [min]	VN ₂ [l]	X ₁	ln(c ₁) [mol/l]	dc ₁ /dt[mol/l/min]	ln(dc ₁ /dt)
0	0	0	0.064851		
1	1.66	0.055101	0.008174	0.058793	-2.83373
2	3.15	0.104559	-0.045589	0.052772	-2.94177
3	4.49	0.149039	-0.096537	0.047459	-3.04788
4	5.71	0.189535	-0.145296	0.043209	-3.1417
5	6.81	0.226048	-0.191394	0.038959	-3.24524
6	7.82	0.259573	-0.235677	0.035772	-3.3306
7	8.74	0.290111	-0.277795	0.032584	-3.42393

$$X_1 = \frac{PV_{N_2}}{RT} \frac{1}{n_1^o}$$

$$c_1 = c_1^o (1 - X_1)$$

$$\left(\frac{dc_1}{dt} \right)_{t_i} \cong \left(\frac{c_1(t_i) - c_1(t_{i-1})}{t_i - t_{i-1}} \right)$$



Integral method

Non linear weighted least squares - Gauss-Newton method

Objective function

$$\Phi(k, n) = \sum_{i=1}^{NEXP} w_i \left[X_1^{EXP}(t_i) - X_1^{MODEL}(t_i, k, n) \right]^2$$

Model

$$\frac{dX_1^{MODEL}}{dt} = k (c_1^o)^{n-1} (1 - X_1^{MODEL})^n$$

$$t = 0, X_1^{MODEL} = 0$$

$X_1^{EXP}(t_i)$ – experimental values of conversion

at $t = t_i$

$X_1^{MODEL}(t_i, k, n)$ – calculated values of conversion

at $t = t_i$ and for given k, n .

w_i weights $\cong \frac{1}{\sigma_i^2}$

Number of Experiments..... 8
 Number of Parameters..... 2
 Number of Responses..... 1
 Number of Settings..... 1

EXIT LSGREG: SOLUTION FOUND. MODEL No. 1

ASYMPTOTIC STATISTICAL ANALYSIS

SOURCE	DF	SUM SQUARES	MEAN SQUARES	F VALUE	F TABLE
REGRESSION.....	1	6.5209E+01	6.5209E+01	8.391E+06	5.99
RESIDUAL.....	6	4.6629E-05	7.7715E-06		
CORRECTED TOTAL.....	7	6.5209E+01			

R-SQUARE..... 1.00000
 ADJUSTED R-SQUARE..... 1.00000
 AVERAGE ABSOLUTE % RESIDUAL.... 0.06%

ESTIMATED PARAMETERS..... 2
 AKAIKE INFORMATION CRITERION... -10.55

PARAMETER STATE	USER ESTIMATES	OPTIMAL ESTIMATES	t-VALUE	STANDARD DEVIATION	ASYMPTOTIC 95% CONFIDENCE INTERVALS
PAR(1) 1	1.0000E+00	5.4129E-02	2.1074E+03	2.5685E-05	5.4129E-02 +- 6.319E-05
PAR(2) 1	1.1000E+00	2.0238E+00	3.4459E+02	5.8730E-03	2.0238E+00 +- 1.445E-02

ASYMPTOTIC CORRELATION MATRIX

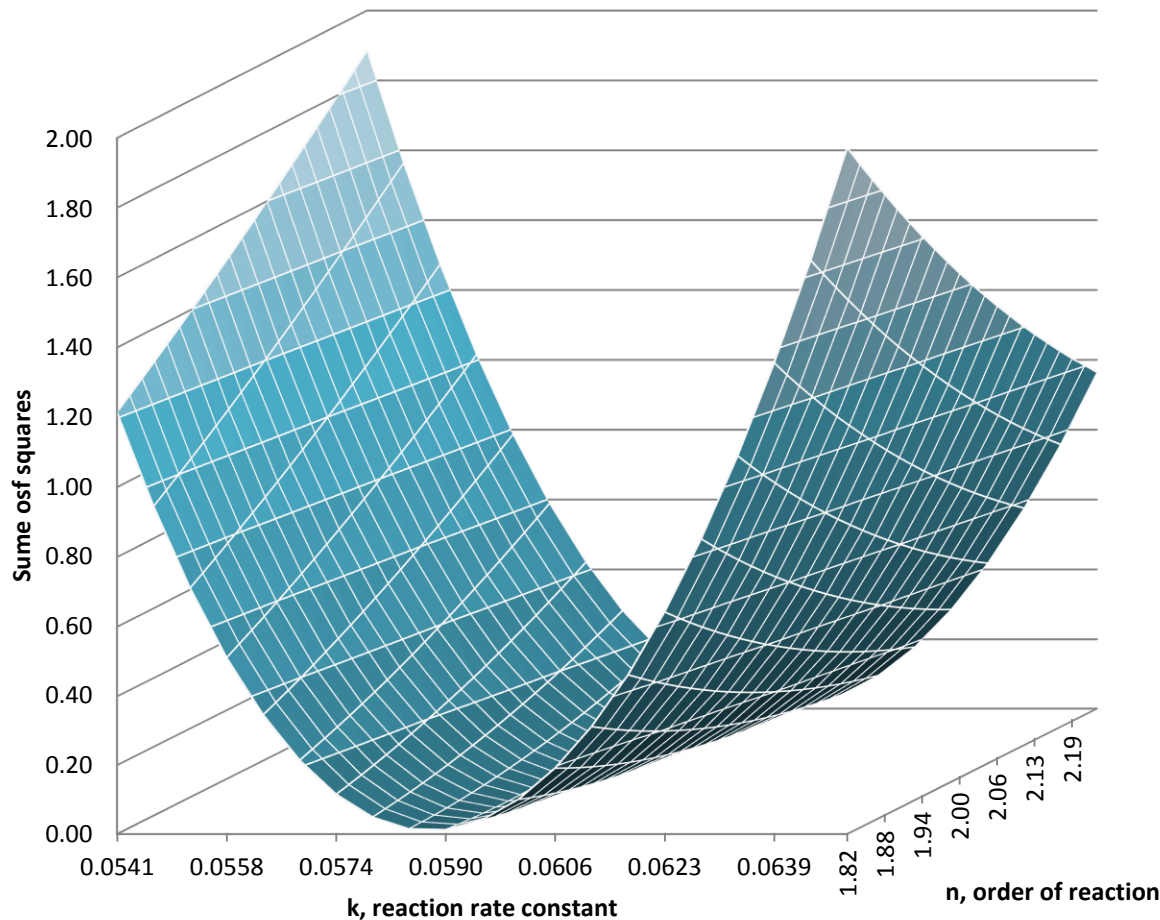
1.000
 0.874 1.000

EVENT	OBSERVED	PREDICTED	RESIDUALS	LOW-VALUE	UPP-VALUE	STD. RSD	LEVERAGE
1	0.0000E+00	0.0000E+00	0.0000E+00	-6.8589E-03	6.8589E-03	0.0000	0.0000
2	1.6600E+00	1.6628E+00	2.7693E-03	1.6554E+00	1.6701E+00	1.0727	0.1425
3	3.1500E+00	3.1514E+00	1.3906E-03	3.1436E+00	3.1591E+00	0.5876	0.2793
4	4.4900E+00	4.4919E+00	1.9479E-03	4.4842E+00	4.4997E+00	0.8263	0.2849
5	5.7100E+00	5.7056E+00	-4.4440E-03	5.6980E+00	5.7131E+00	-1.8056	0.2205
6	6.8100E+00	6.8095E+00	-5.0915E-04	6.8020E+00	6.8170E+00	-0.2031	0.1913
7	7.8200E+00	7.8180E+00	-1.9751E-03	7.8102E+00	7.8258E+00	-0.8419	0.2919
8	8.7400E+00	8.7431E+00	3.0533E-03	8.7344E+00	8.7517E+00	1.7096	0.5896*

NUMBER OF ITERATIONS..... 20
 NUMBER OF FUNCTION CALLS..... 95

Athena Visual Studio
<http://www.athenavisual.com/>

Sum of squares of deviations as a function of parameters k and n



Very flat objective function in the direction of parameter n → further experimental data needed to obtain reliable value of n

Further reading

Yonathan Bard: Nonlinear Parameter Estimation, McGraw-Hill, 1967

Uveřejněné materiály jsou určeny studentům Vysoké školy chemicko-technologické v Praze jako studijní materiál. Některá textová i obrazová data v nich obsažená jsou převzata z veřejných zdrojů. V případě nedostatečných citací nebylo cílem autora/ů záměrně poškodit event. autora/y původního díla.

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6. Energy balance on chemical reactors



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YOUTH AND SPORTS

Most of reactions are not carried out isothermally

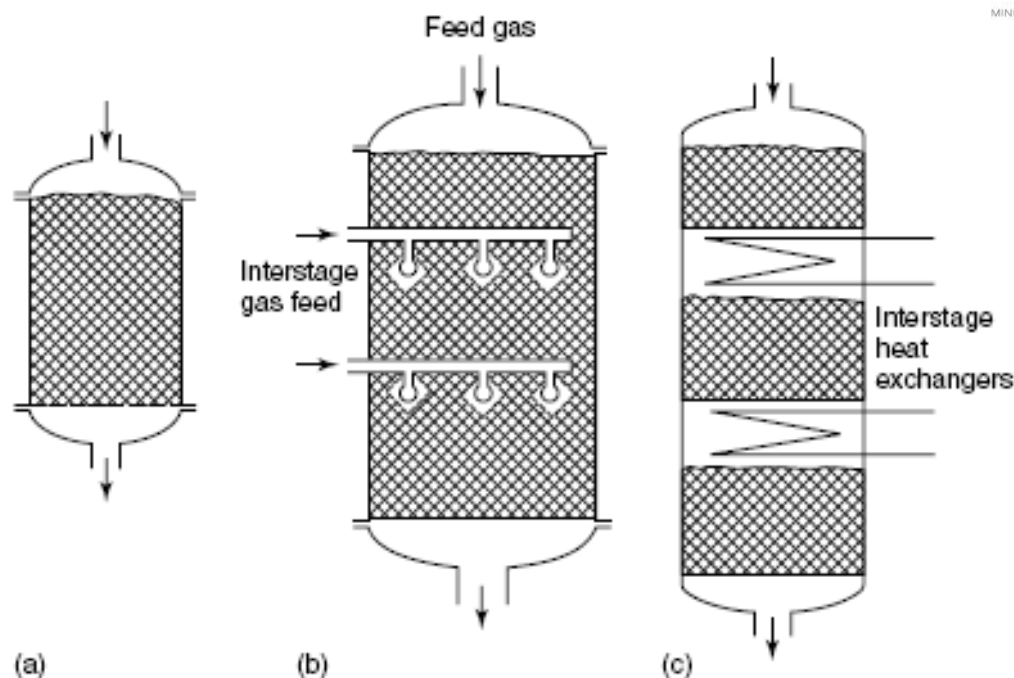


Fig. 12 Development of fixed-bed reactors. (a) Single-bed adiabatic packed-bed reactor; (b) adiabatic reactor with interstage gas feed (ICI concept); (c) multi-bed adiabatic fixed-bed reactor with interstage heat exchange.

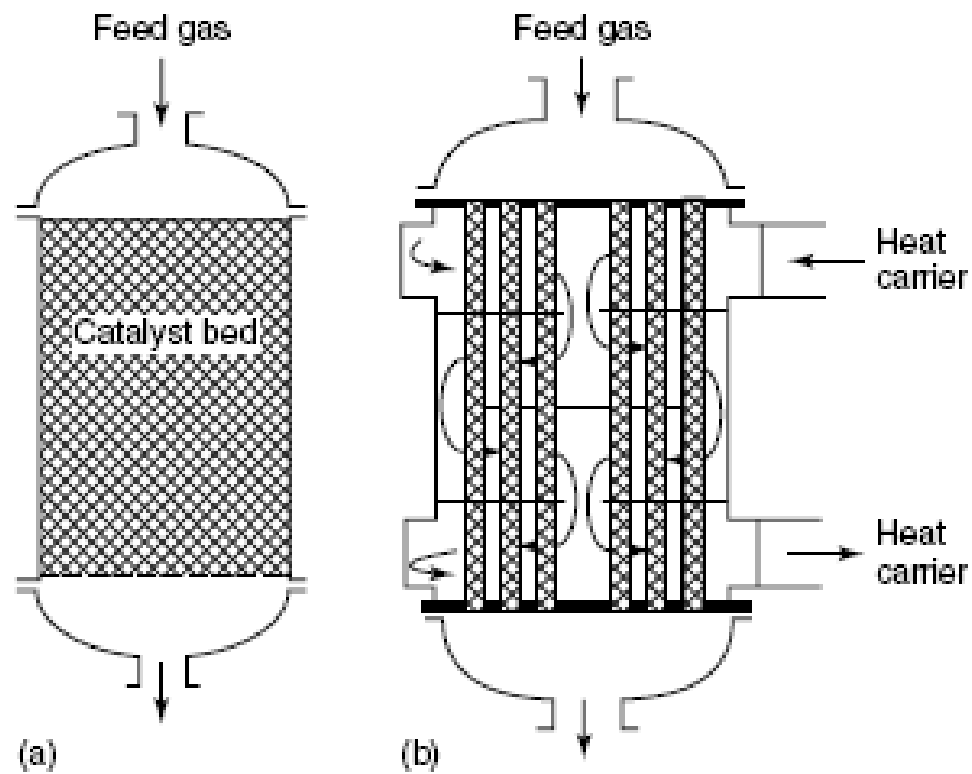


Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.

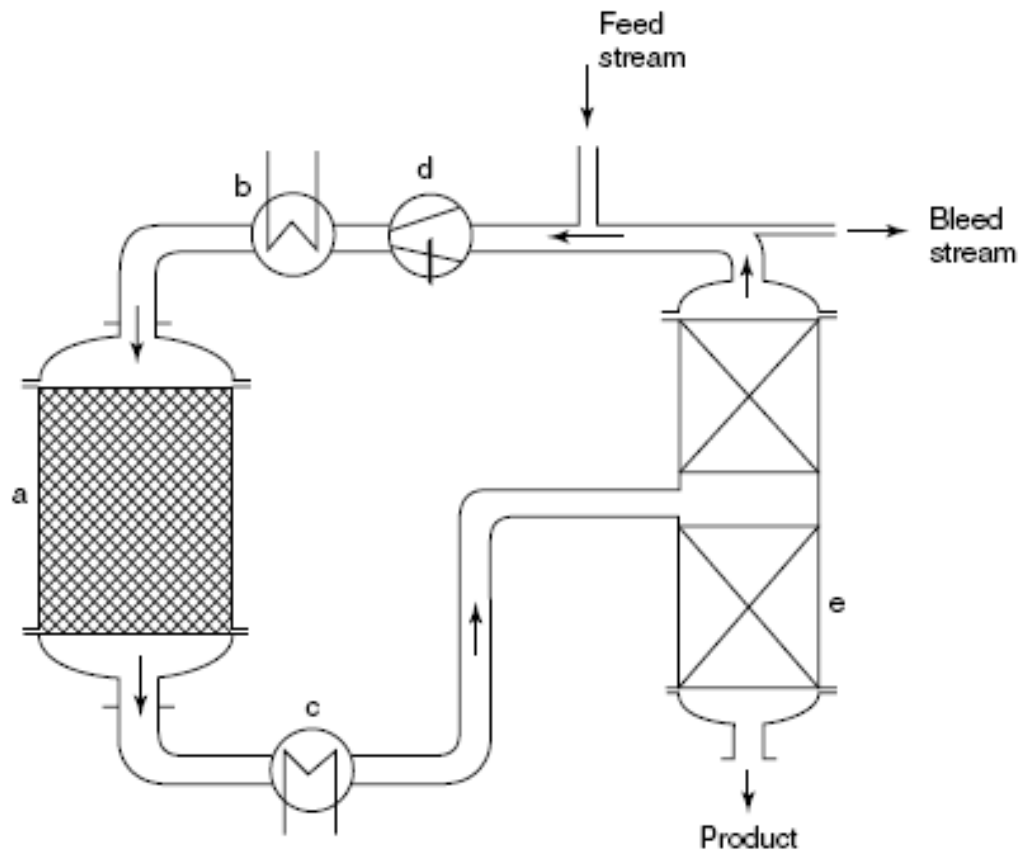
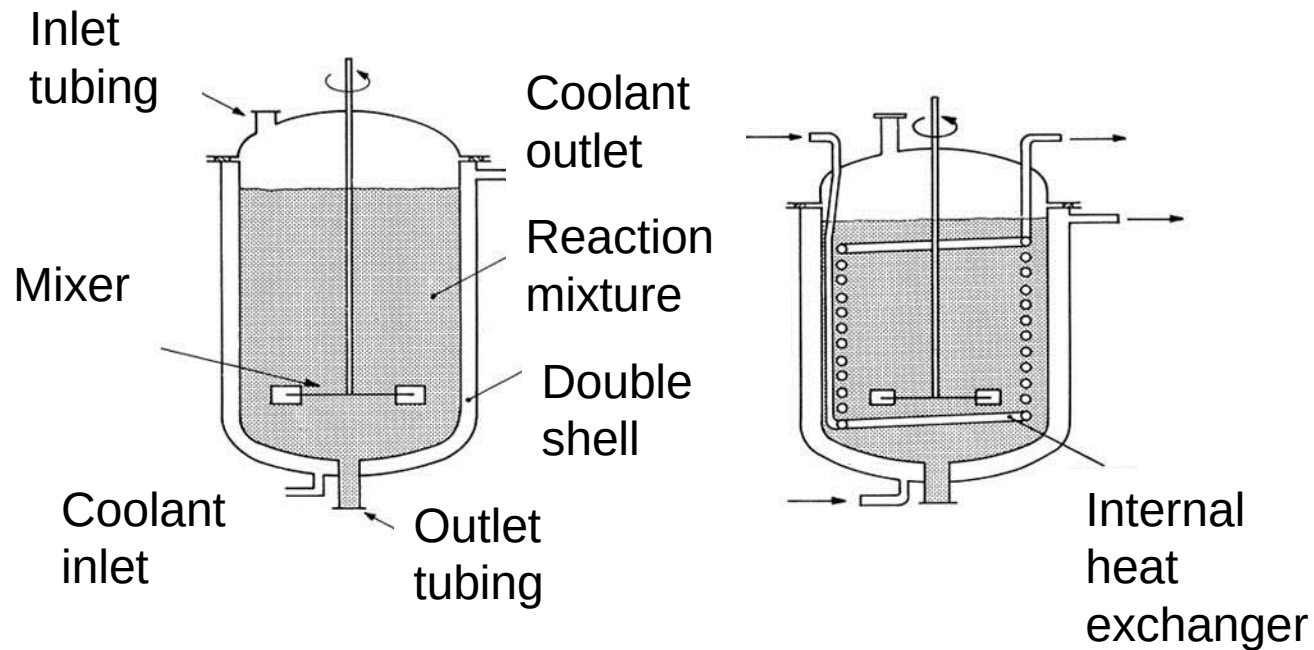


Fig. 2 Reaction cycle for synthesis reactions with incomplete conversion. (a) Fixed-bed reactor; (b) feed preheater; (c) exit cooler; (d) recirculation compressor; (e) separation device.

BATCH or CSTR heated (cooled) reactors



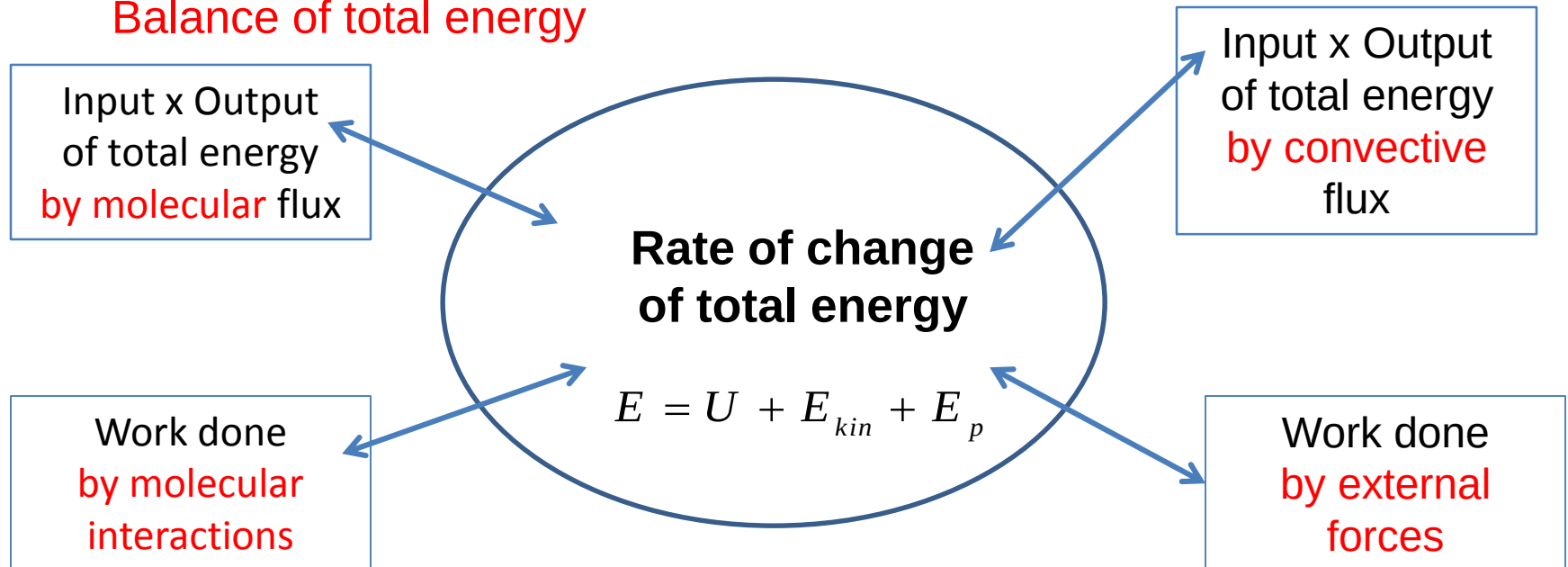
The balance of total energy involves:

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

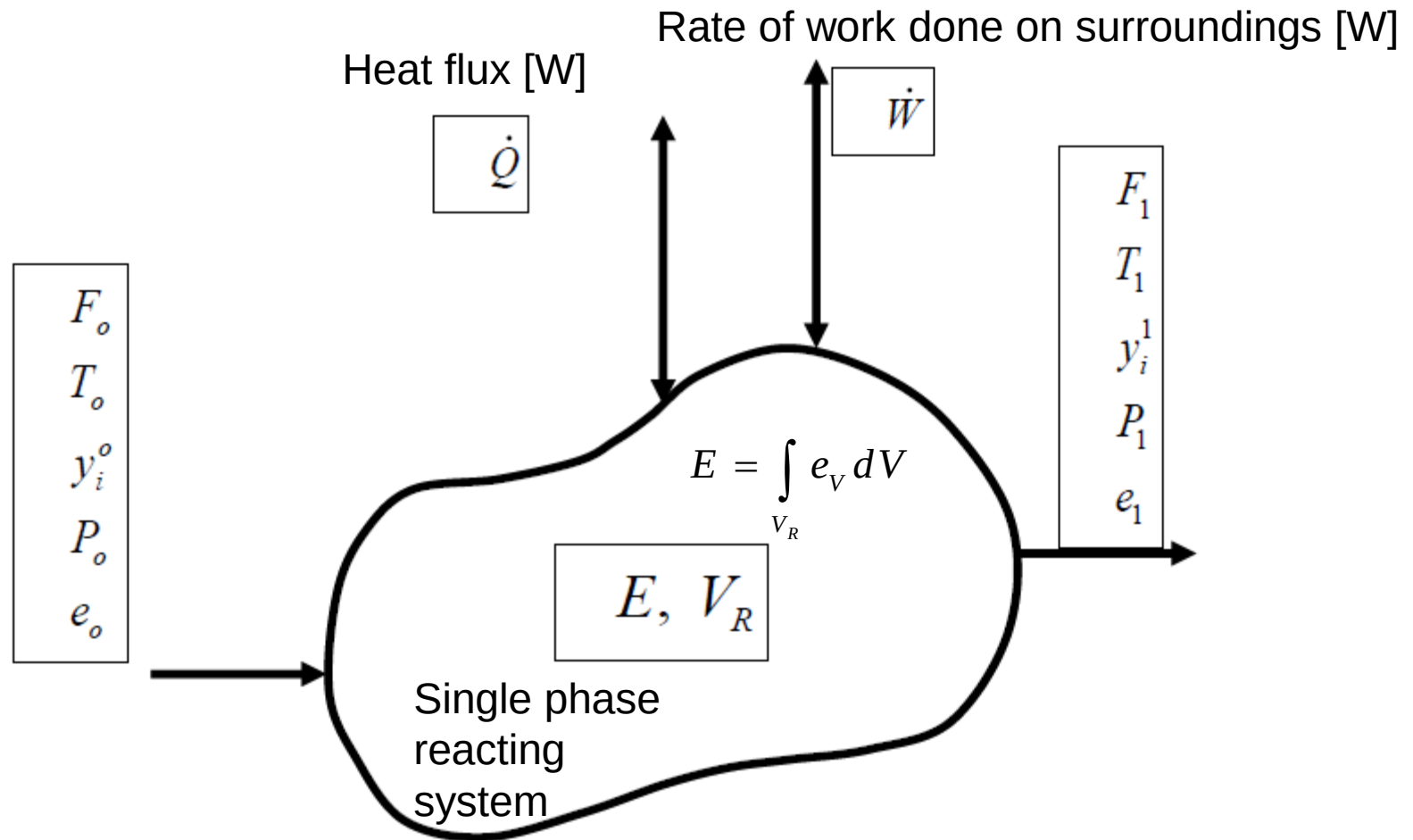
Transformation of various kinds of energy

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 [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

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

- 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

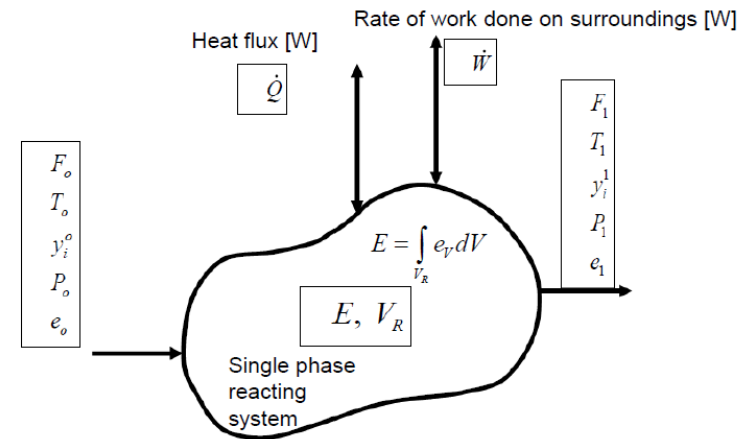
$$\frac{dH}{dt} = \frac{dU}{dt} + V_R \frac{dP}{dt} + P \frac{dV_R}{dt} \longrightarrow \frac{dH}{dt} = V_R \frac{dP}{dt} + F_o h_{mo} - F_1 h_{m1} + \dot{Q}$$

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 $\alpha_p \cong 0, c_p \cong c_v$

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

liquid (condensed) systems

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

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

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

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

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

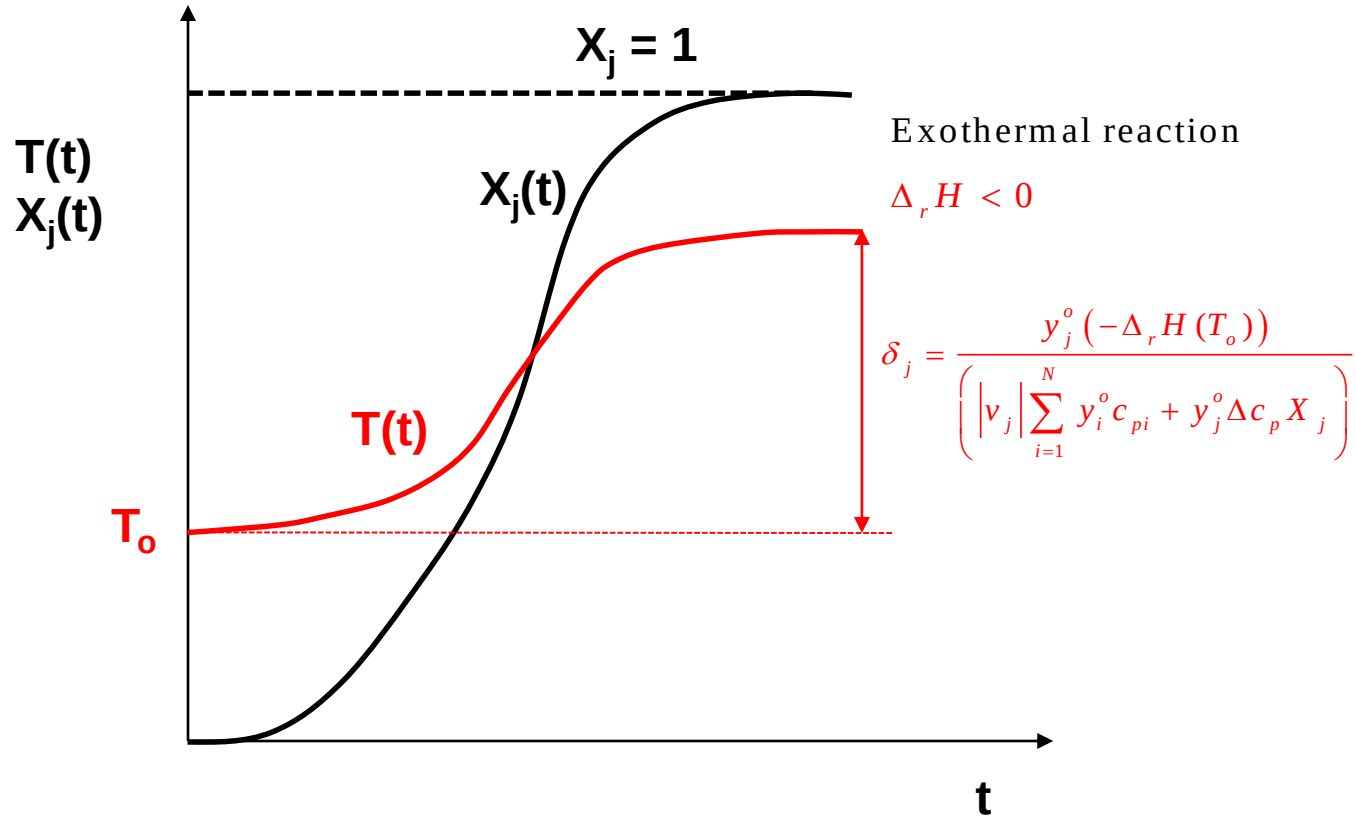
Assuming that $c_{pi} = \text{const} \Rightarrow \Delta c_p = \text{const}$

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

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

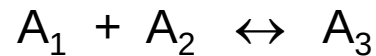
the adiabatic rise of temperature

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})

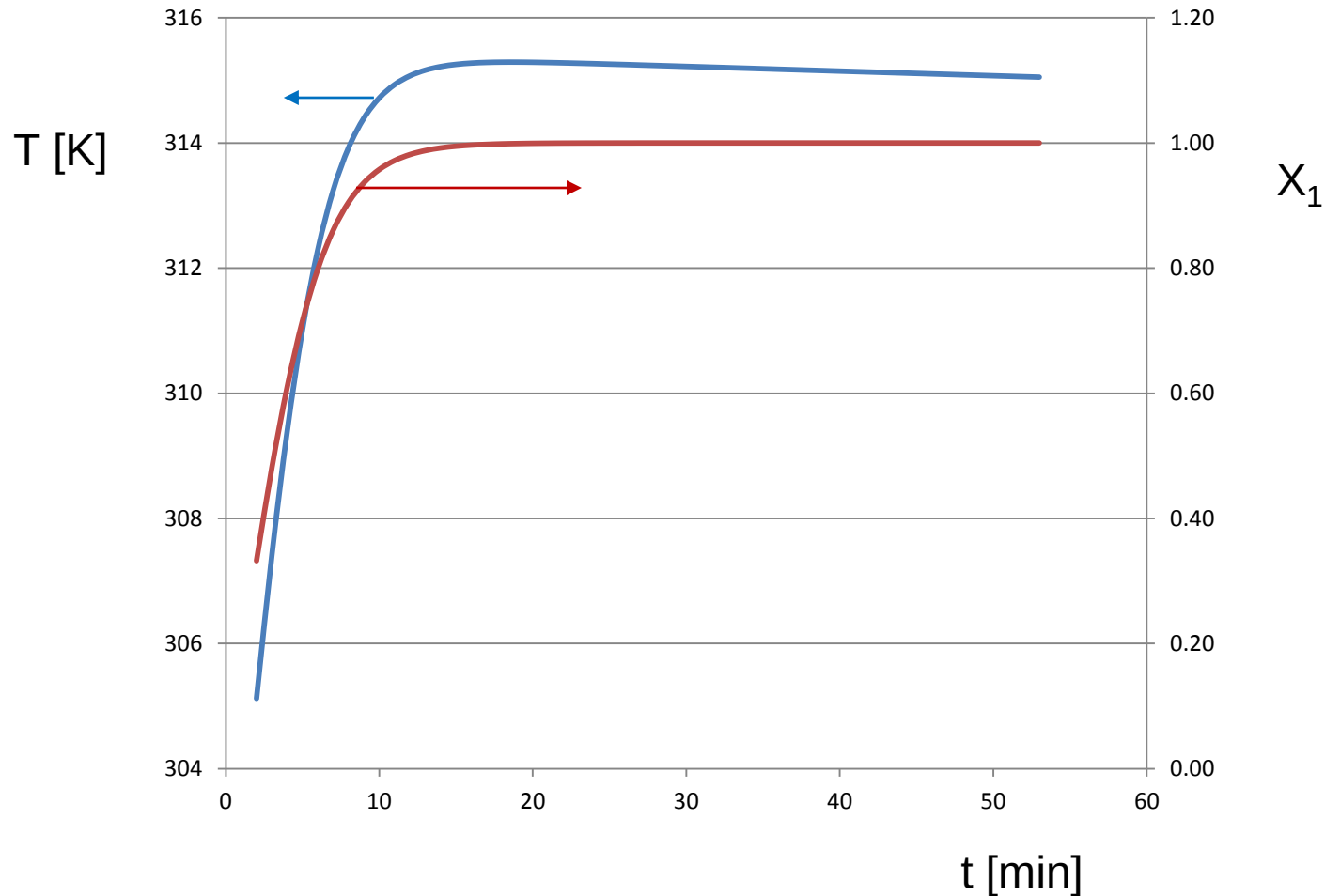
$$R = 8.31446 \text{ J.mol}^{-1}.\text{K}^{-1}$$

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

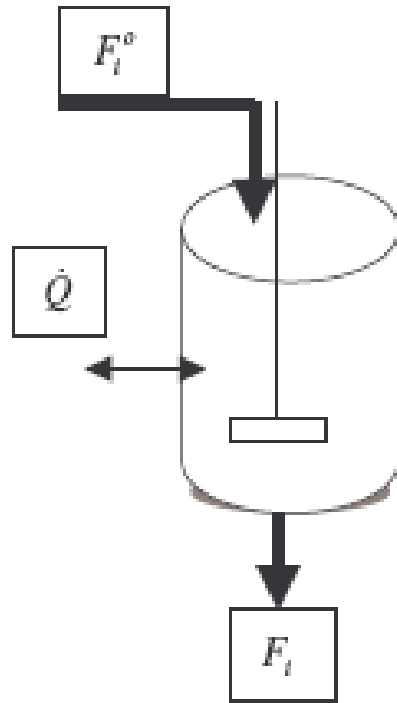
By numerical integration we get

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

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



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

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

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

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

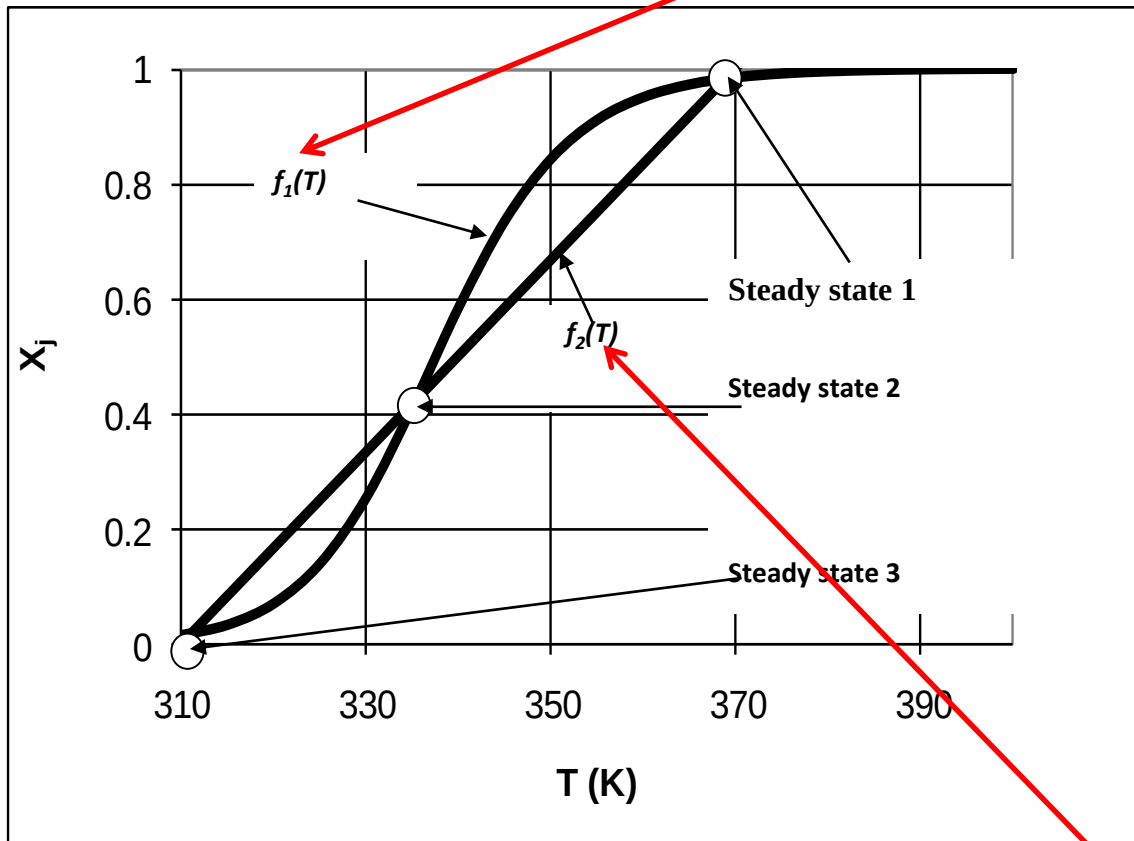
2 nonlinear algebraic equations for unknown T and X_j

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

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

Multiple steady states of adiabatic CSTR (exothermal reaction)

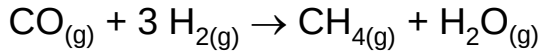
$$F_j^o X_j + v_j r_V(X_j, T) V_R = 0 \Rightarrow X_j = f_1(T)$$



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

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:

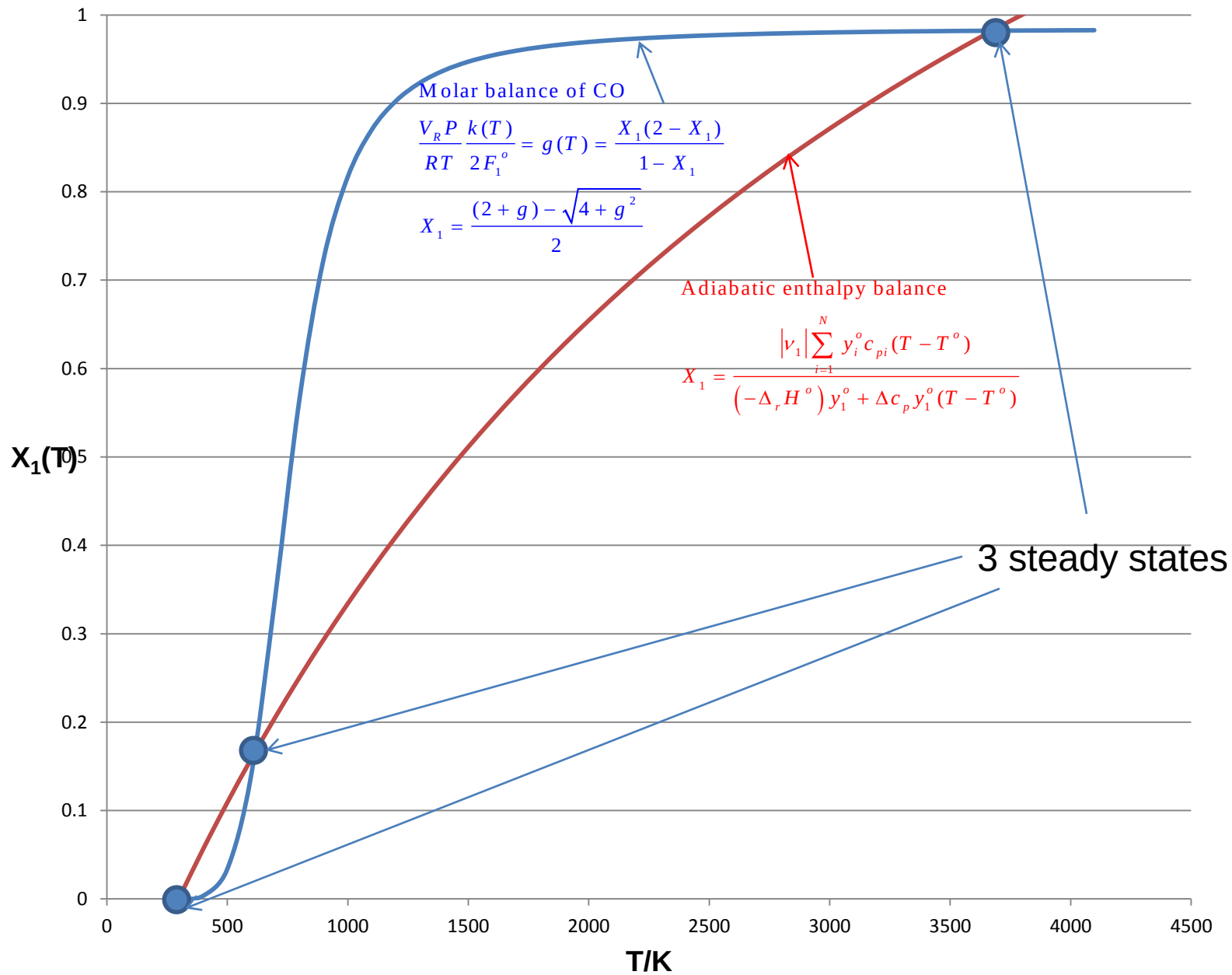
$$C_{\text{CO}}(\text{in}) = 0.0102 \text{ mol/liter} \quad C_{\text{H}_2}(\text{in}) = 0.0306 \text{ mol/liter}$$

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



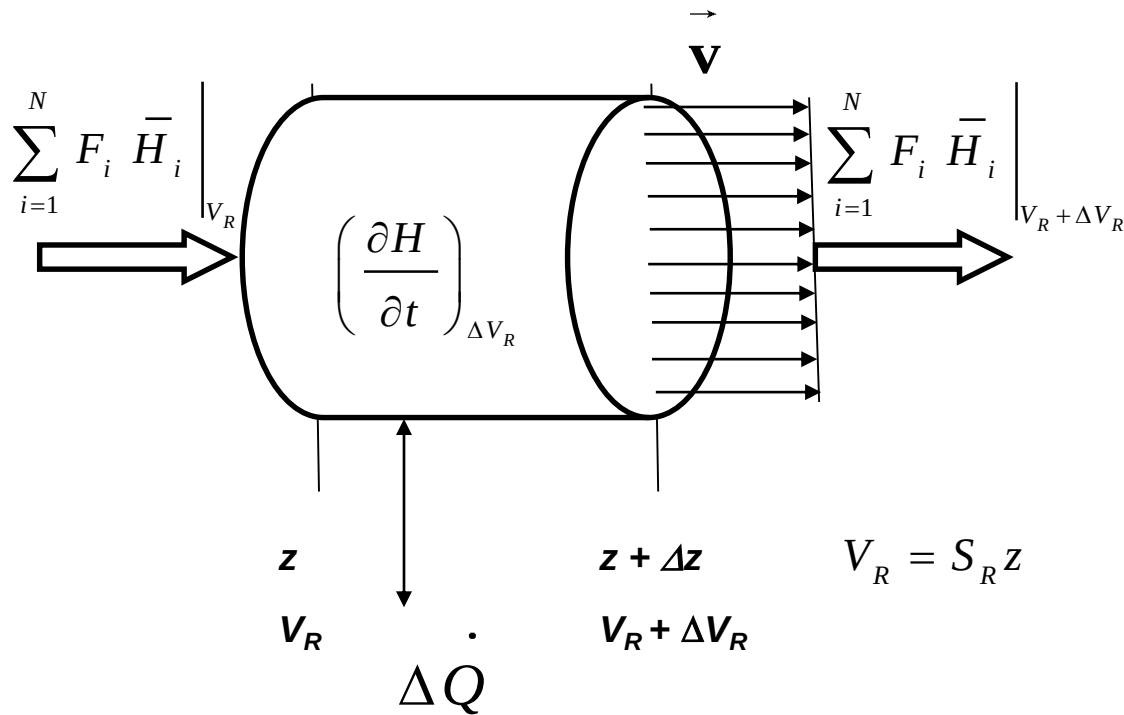
Reaction rate:

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

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)



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

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

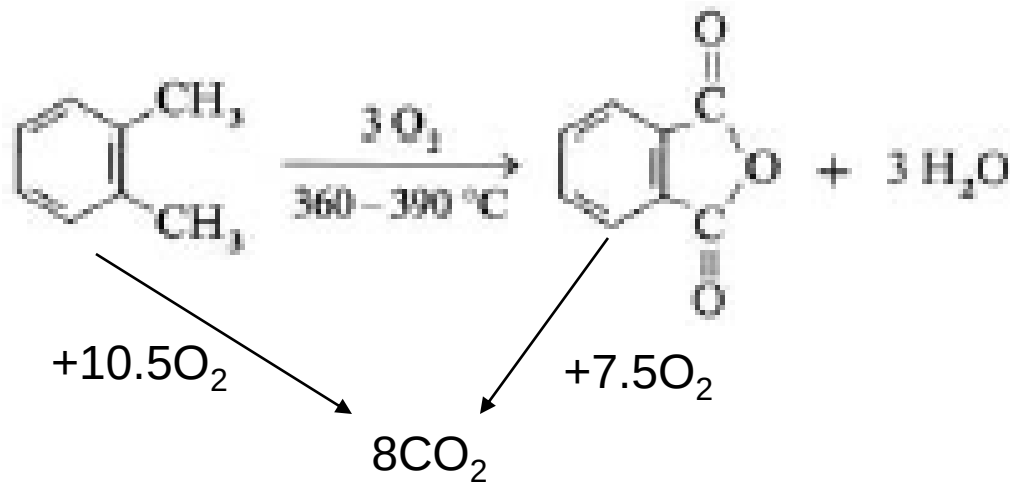
$$= \sum_{k=1}^{NR} \Delta_r H_k r_{V,k} + \frac{dT}{dV_R} \sum_{i=1}^N F_i c_{pi} = \frac{d\dot{Q}}{dV_R}$$

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

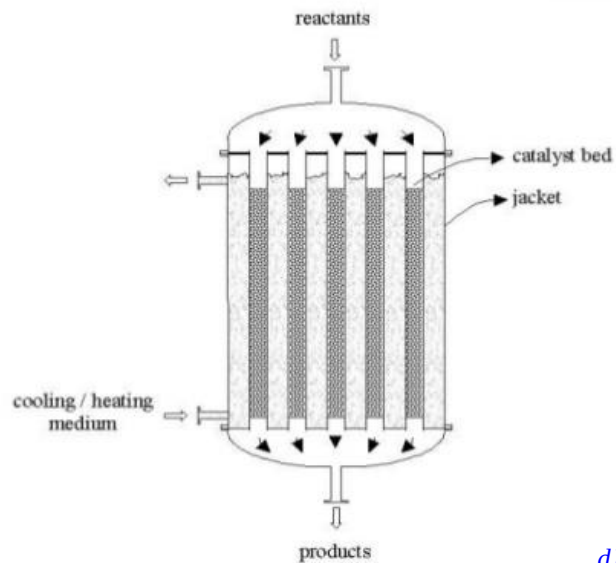
$$\frac{dT}{dV_R} = \frac{1}{\sum_{i=1}^N F_i c_{pi}} \left[\sum_{k=1}^{NR} (-\Delta_r H_k) r_{V,k} + \frac{4\omega}{d_R} (T_e - T) \right] \quad \frac{dS_t}{dV_R} = \frac{\pi d_R dz}{\pi \frac{d_R^2}{4} dz}$$

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

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

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

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

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

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

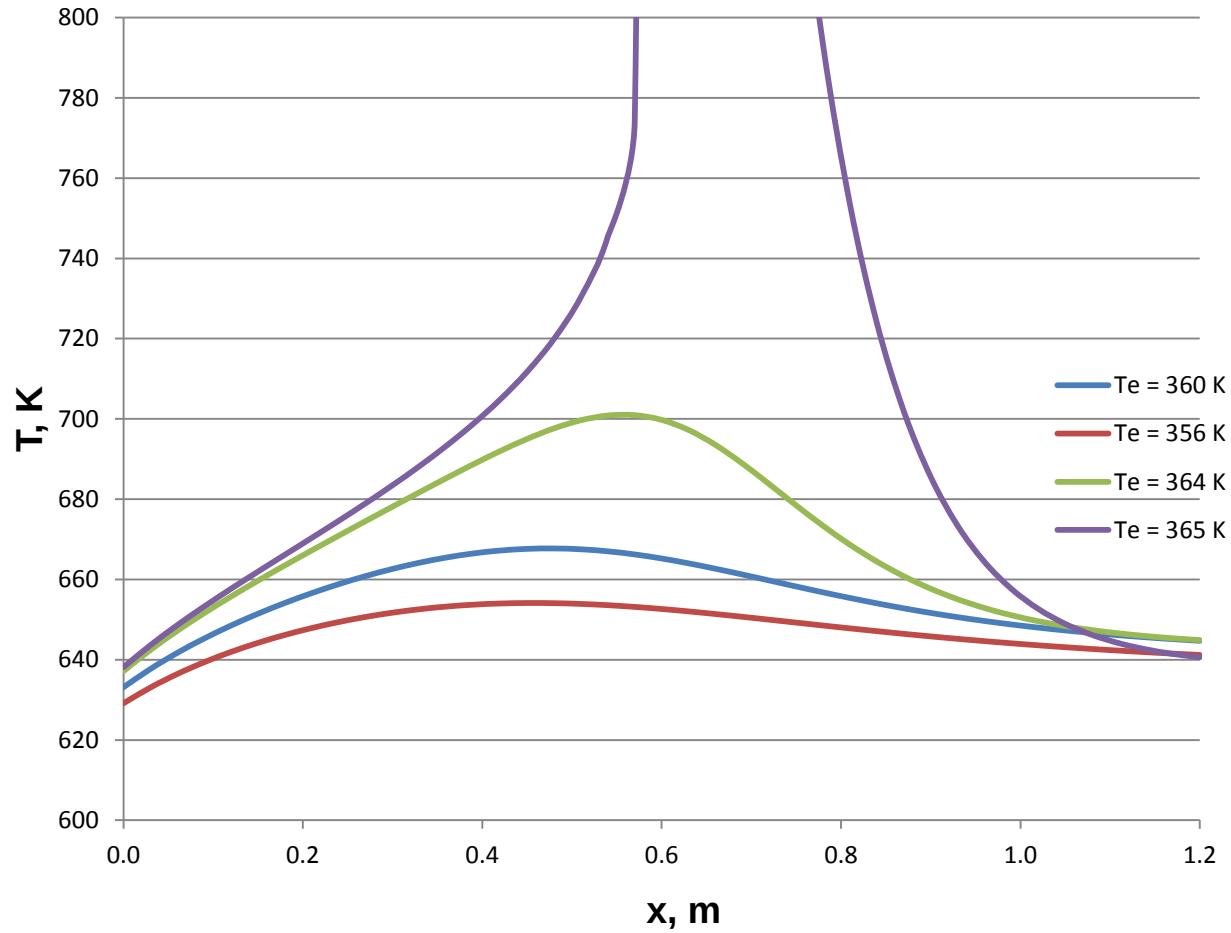
Enthalpy balance

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

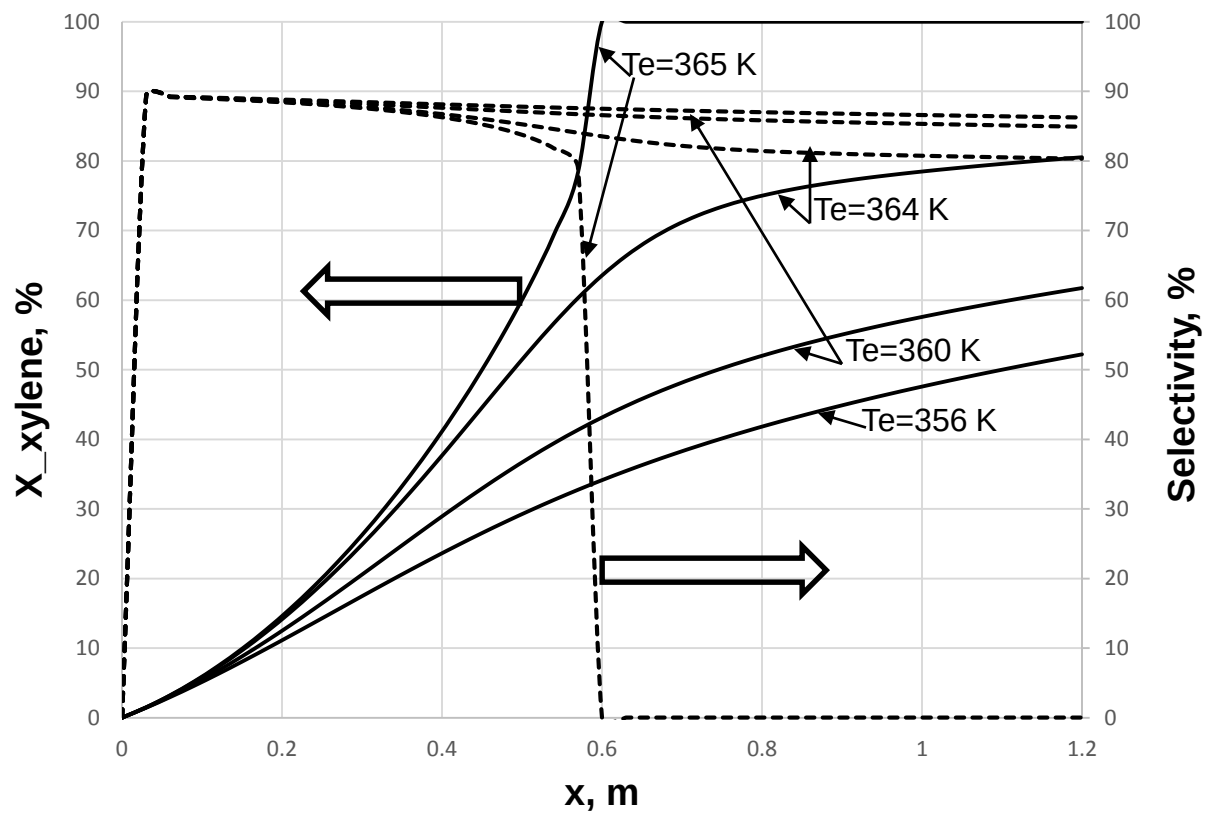
Numerical values of parameters

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

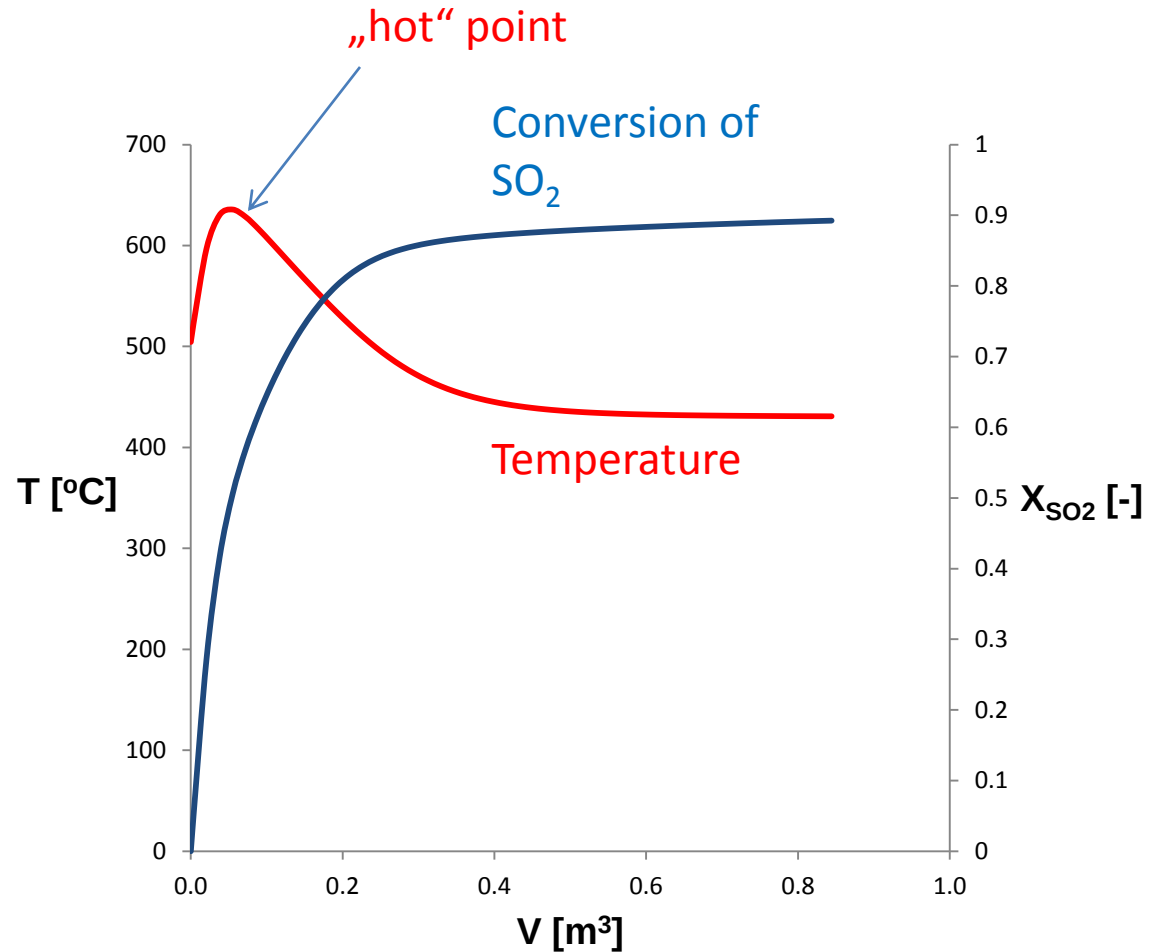
„Stiff“ solvers

MATLAB

www.netlib.org

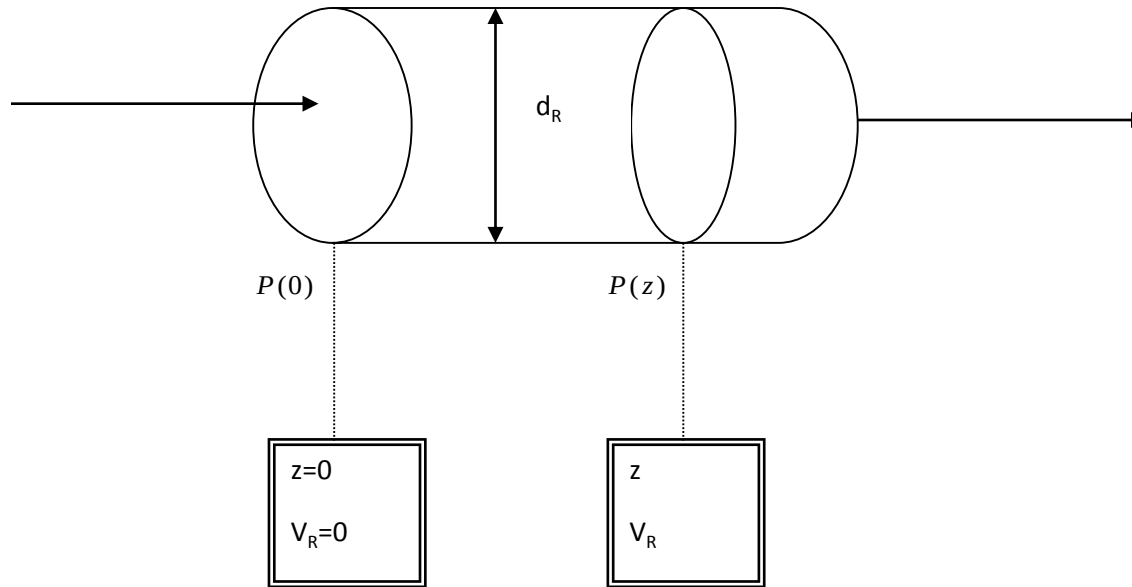
www.athenavisual.com

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

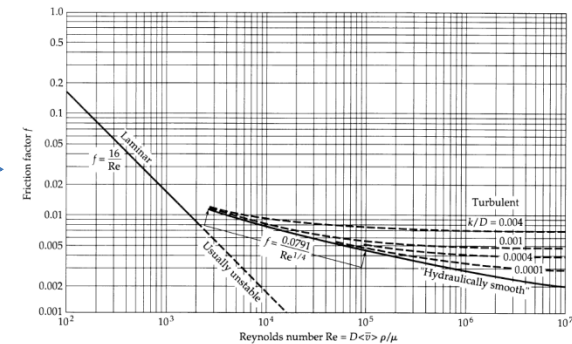


Fig. 6.2-2. Friction factor for tube flow (see definition of f in Eqs. 6.1-2 and 6.1-3. [Curves of L. F. Moody, Trans. ASME, 66, 671-684 (1944) as presented in W. L. McCabe and J. C. Smith, Chemical Engineering, McGraw-Hill, New York (1954).]

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.

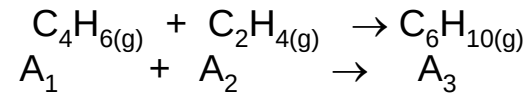
Data:

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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7. Mass and Energy Balances on Plug Flow Packed Bed Reactor (PFPBR)



- In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame.
- Material and energy balances are required for both the fluid, which occupies the interstitial region between catalyst particles, and the catalyst particles, in which the reactions occur.
- The following figure presents several views of the fixed-bed reactor. The species production rates in the bulk fluid are *essentially zero*. That is the reason we are using a catalyst.
- Essentially all reaction occurs within the catalyst particles. The fluid in contact with the external surface of the catalyst pellet is denoted with subscript s .

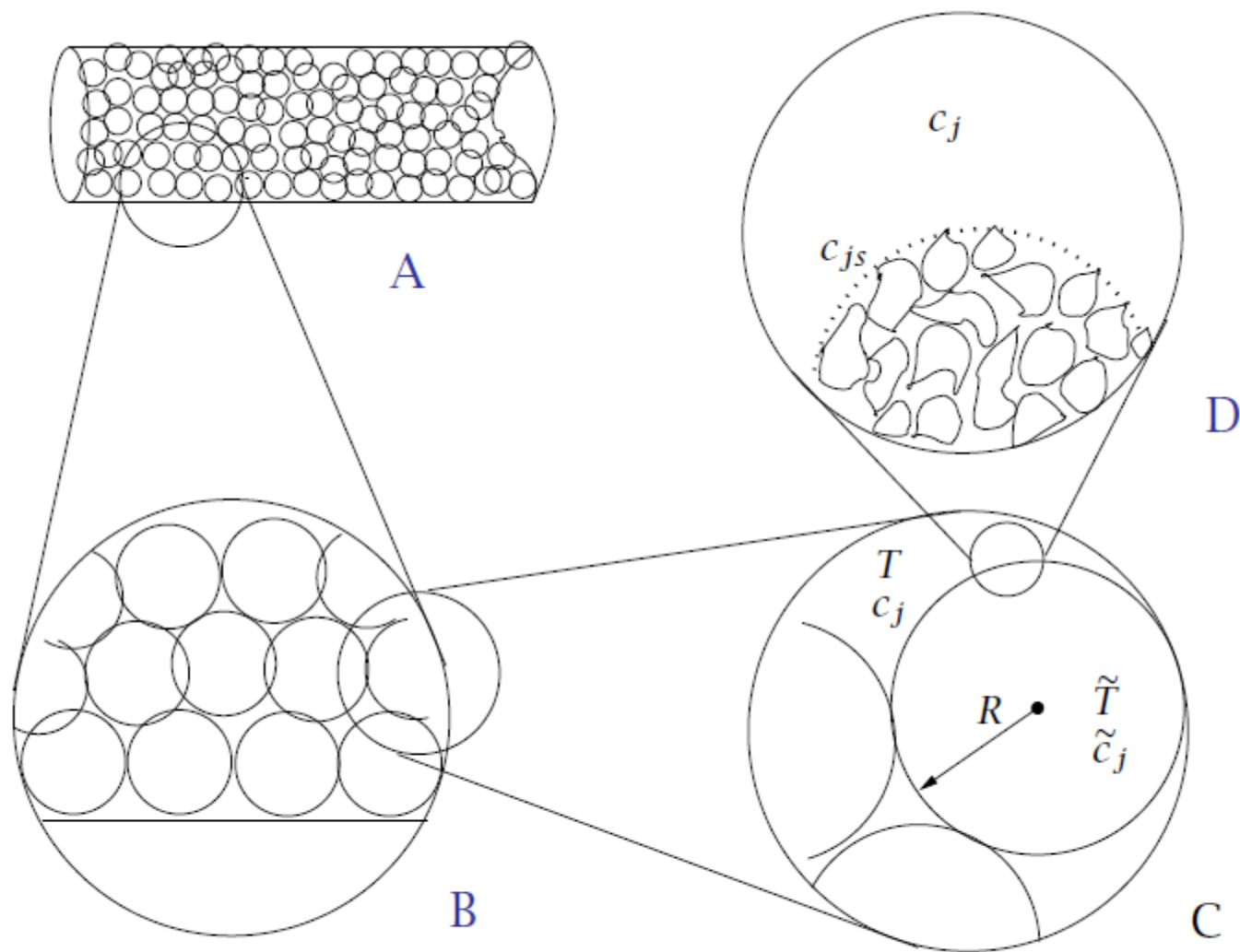


Figure 1: Expanded views of a fixed-bed reactor.

During any catalytic reaction the following steps occur:

1. transport of reactants and energy from the bulk fluid up to the catalyst pellet exterior surface,
2. transport of reactants and energy from the external surface into the porous pellet,
3. adsorption, chemical reaction, and desorption of products at the catalytic sites,
4. transport of products from the catalyst interior to the external surface of the pellet, and
5. transport of products into the bulk fluid.

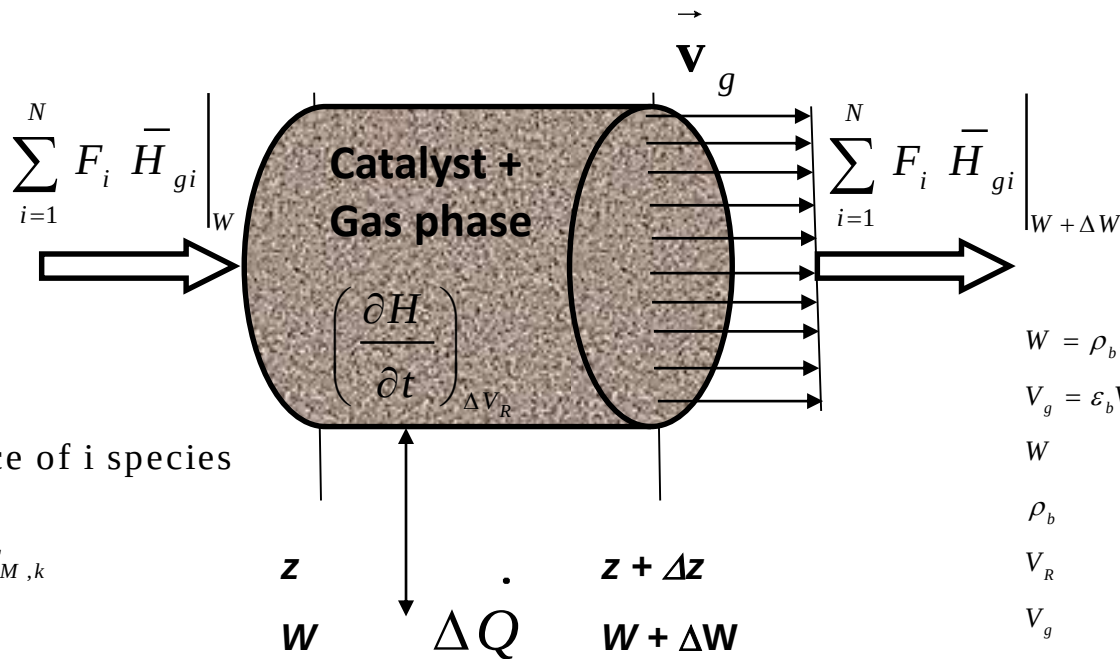
The coupling of transport processes with chemical reaction can lead to concentration and temperature gradients within the pellet, between the surface and the bulk, or both.

- In the fixed-bed reactor, we keep track of two phases. The fluid-phase streams through the bed and transports the reactants and products through the reactor.
- The reaction-diffusion processes take place in the solid-phase catalyst particles.
- The two phases communicate to each other by exchanging mass and energy at the catalyst particle exterior surfaces.

We make the following assumptions:

1. Uniform catalyst pellet exterior. Particles are small compared to the length of the reactor.
2. Plug flow in the bed, no radial profiles.
3. Neglect axial diffusion in the bed.
4. Steady state.

Balances on Plug Flow Packed Bed Reactor (PFPBR)



Molar balance of i species

$$\frac{dF_i}{dW} = \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

$$W = \rho_b S_R z = \rho_b V_R \quad V_R = V_g + V_s$$

$$V_g = \varepsilon_b V_R \quad V_s = (1 - \varepsilon_b) V_R$$

W mass of catalyst [kg]

ρ_b bulk density of the catalyst [kg/m^3]

V_R total volume of reactor [m^3]

V_g volume of the gas phase in reactor [m^3]

V_s volume of the catalyst in reactor [m^3]

ε_b bed porosity, $\varepsilon_b = \frac{V_g}{V_R}$ [-]

Overall enthalpy balance involved both gas and solid phase

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

in the steady state

$$0 = \sum_{i=1}^N F_i \bar{H}_{gi} \Big|_W - \sum_{i=1}^N F_i \bar{H}_{gi} \Big|_{W + \Delta W} + \Delta \dot{Q} \Rightarrow \frac{d}{dW} \sum_{i=1}^N F_i \bar{H}_{gi} = \frac{d\dot{Q}}{dW}$$

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

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

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

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

Circular cross section

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

$$\frac{dS_t}{dW} = \frac{\pi d_R dz}{\rho_b \pi \frac{d_R^2}{4} dz} = \frac{4}{\rho_b d_R}$$

Enthalpy balance

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

Initial conditions

$$W = 0, F_i = F_i^o, T = T^o$$

Molar balance of i species

$$\frac{dF_i}{dW} = \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

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

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

$$\frac{dX_j}{dW} = -\frac{\nu_j}{F_j^o} r_M(X_j, T) = \frac{|\nu_j|}{F_j^o} r_M(X_j, T)$$

$W = 0, T = T_o, X_j = 0$

$$\frac{dF_i}{dW} = \nu_i r_M = \frac{\nu_i}{\nu_j} \frac{dF_j}{dW}$$

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

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

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

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

Limiting cases

1. Isothermal reactor

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

$T = T_o$

2. Adiabatic reactor

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

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

Cf. adiabatic BATCH, CSTR and PFR

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]

$$v_f^o = 4\dot{m} / (\rho_f \pi d_R^2)$$

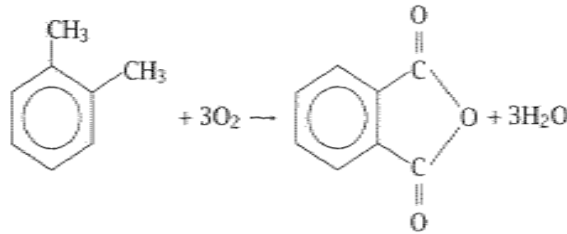
$\dot{m}$ mass flowrate [kg/s]

ε_b bed porosity [-]

d_p catalyst particle (equivalent) diameter [m]

Example

Oxidation of o-xylene to phthalic anhydride¹



The gas phase oxidation is highly exothermic. The reaction is carried out in PFR tube bundles with molten salt circulating as the heat transfer fluid. The o-xylene is mixed with air before entering the PFR. The large excess of oxygen leads to a pseudo-first order rate expression

$$r_v = k(T_o) \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] c_1 \quad A_1 = \text{o-xylene}$$

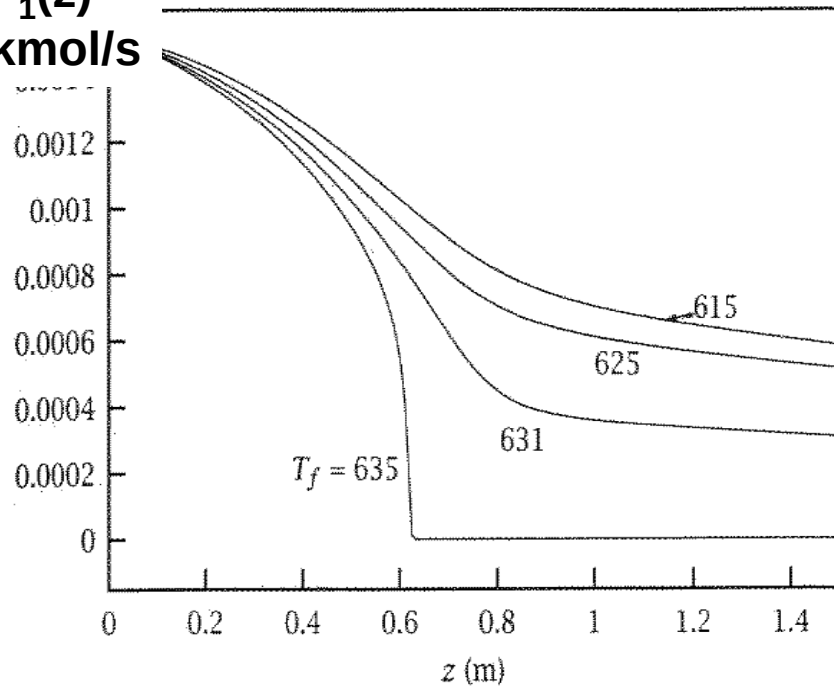
Calculate the temperature and composition profiles.

1. Rawlings, G.B., Ekerdt, J.G., Chemical Reactor Analysis and Design Fundamentals, Nob Hill Publ., Madison, Wisc. 2002.

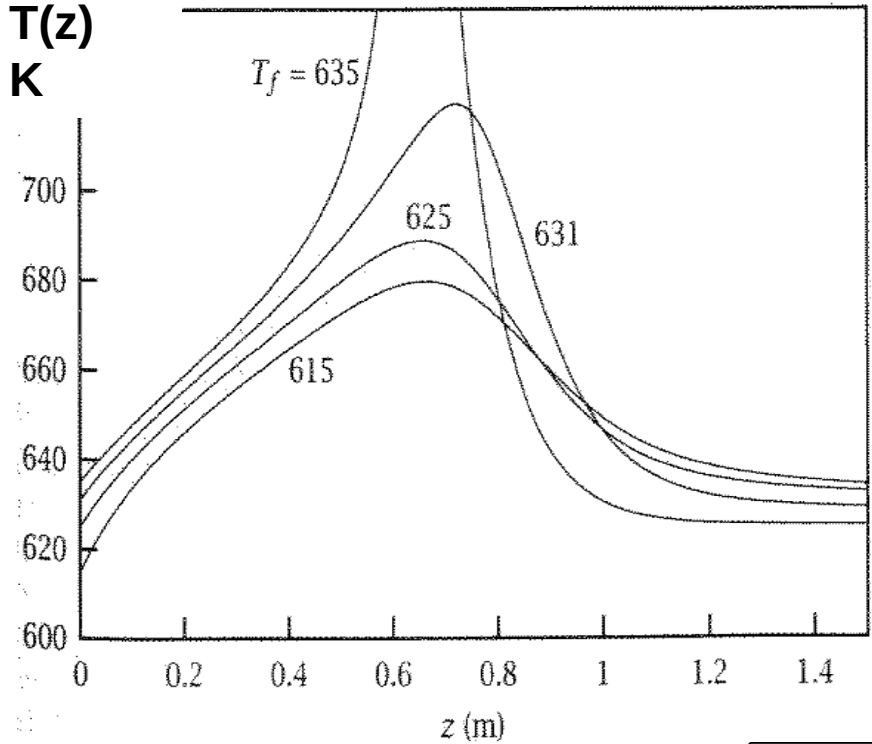
Data

$k(T_o), s^{-1}$	T_o, K	T_m, K	P, bar	L, m	d_R, m
1922.6	625	625	1.01	1.5	0.025
$C_p, kJ/kg/K$	y_1^o	$E/R, K$	$\Delta_r H, kJ/mol$	$G, kg/s$	$\omega, kJ/m^2/s/K$
0.992	0.019	1.3636×10^4	-1.361×10^3	2.6371×10^{-3}	0.373

$F_1(z)$
kmol/s



$T(z)$
K



Heterogeneous non catalytic reactions

- solid – fluid (liquid, gas)

- Dissolution of solids (e.g. $\text{MgCO}_{3(s)} + \text{HNO}_{3(l)}$)
- Chemical Vapor Deposition ($\text{SiH}_{4(g)} \rightarrow \text{Si}_{(s)} + 2\text{H}_2$)
- Sublimation ($\text{U}_{(s)} + 3 \text{F}_{2(g)} \rightarrow \text{UF}_{6(g)}$)
- Reduction of solid oxides ($\text{NiO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Ni}_{(s)} + \text{H}_2\text{O}_{(g)}$)
- Metals oxidation ($\text{Zn}_{(s)} + \text{O}_{2(g)} \rightarrow \text{ZnO}_{(s)}$)
- Catalytic reactions

- liquid – gas

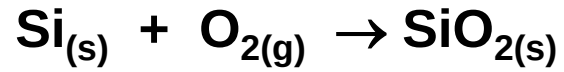
- Dissolution with chemical reaction
 $\text{Cl}_{2(s)} + 2\text{NaOH}_{(l)} \rightarrow \text{NaOCl}_{(l)} + \text{NaCl}_{(l)} + \text{H}_2\text{O}_{(l)}$
 $3\text{NO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{HNO}_{3(l)} + \text{NO}_{(g)}$

- solid – solid

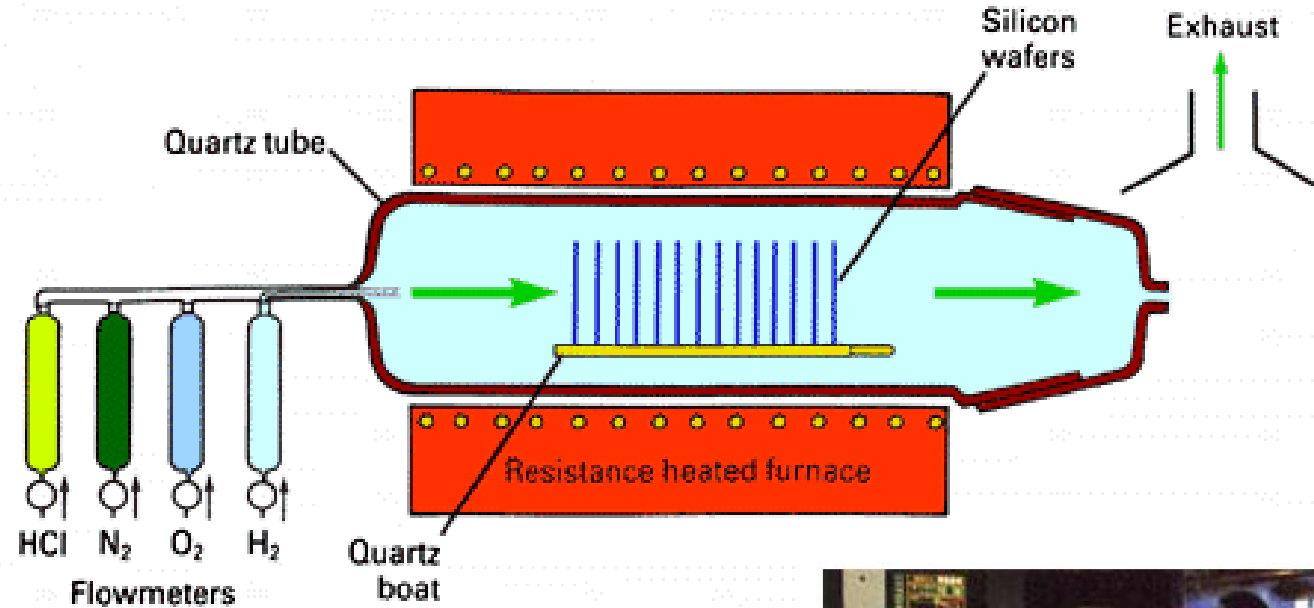
- $\text{CoO}_{(s)} + \text{Al}_2\text{O}_{3(s)} \rightarrow \text{CoAl}_2\text{O}_{4(s)}$

Heat and mass transfer phenomena affect global reaction rate.

Heterogeneous gas-solid reactions

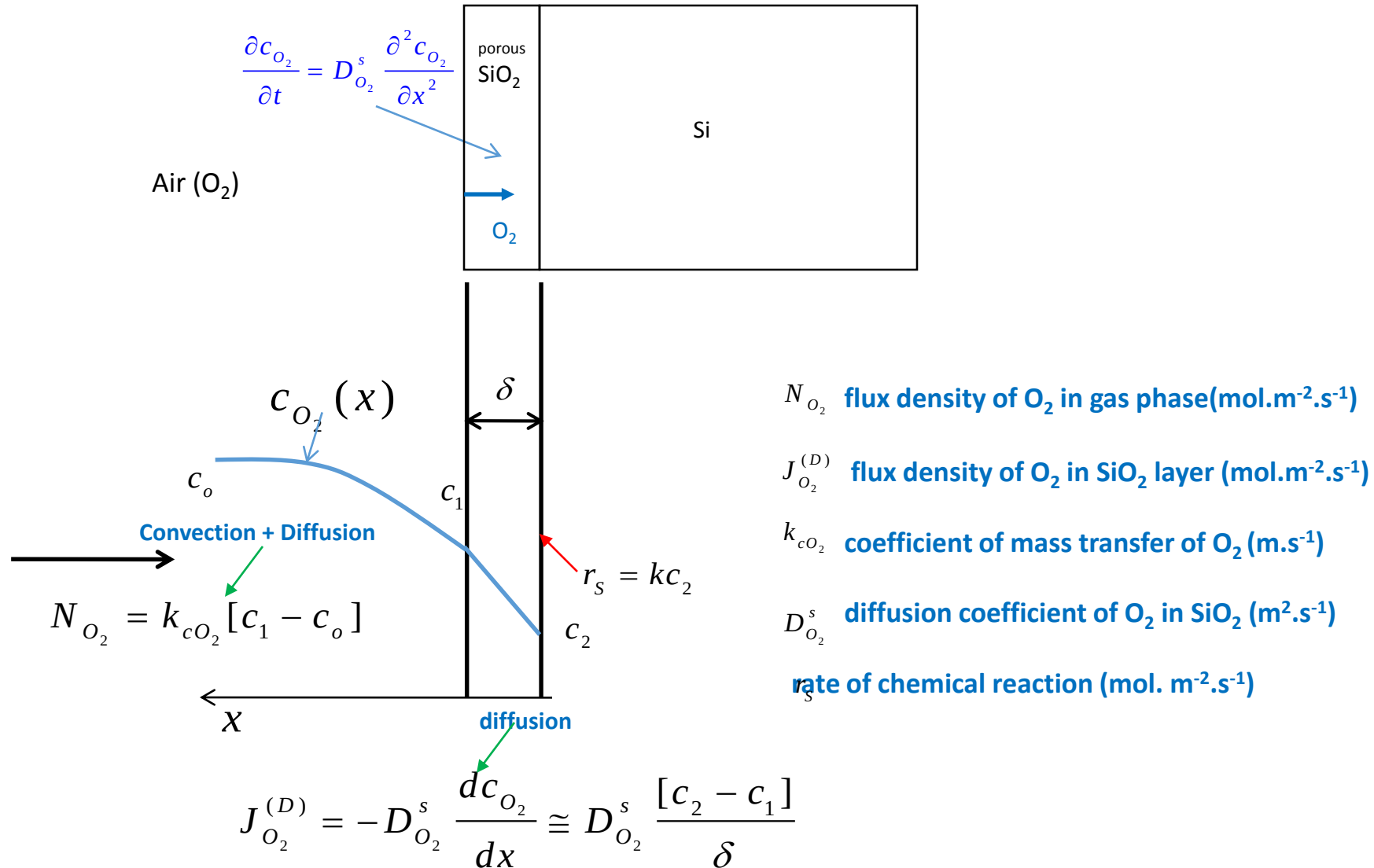
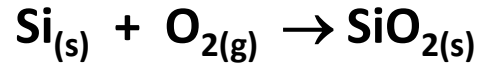


Silicon thermal oxidation is by far most important for silicon devices. It is the key process in modern silicon integrated circuit technology.



Oxidation Furnace
(Silicon Valley Group - Thermco Systems)

Kinetics of gas-solid heterogeneous reaction



Steady state

$$N_{O_2} = J_{O_2}^{(D)} = \nu_{O_2} r_s$$

$$k_{CO_2} [c_1 - c_o] = D_{O_2}^s \frac{[c_2 - c_1]}{\delta} = -k c_2$$

c_1 a c_2 calculation :

$$\left(k_{CO_2} + \frac{D_{O_2}^s}{\delta} \right) c_1 - \frac{D_{O_2}^s}{\delta} c_2 = k_{CO_2} c_o$$

$$-\frac{D_{O_2}^s}{\delta} c_1 + \left(k + \frac{D_{O_2}^s}{\delta} \right) c_2 = 0$$

$$c_1 = \frac{k_{CO_2} \left(k + \frac{D_{O_2}^s}{\delta} \right)}{k \cdot k_{CO_2} + \frac{D_{O_2}^s}{\delta} (k_{CO_2} + k)} c_o$$

$$c_2 = \frac{k_{CO_2} \frac{D_{O_2}^s}{\delta}}{k \cdot k_{CO_2} + \frac{D_{O_2}^s}{\delta} (k_{CO_2} + k)} c_o$$

SiO_2 layer thickness and Si conversion :

reaction rate

$$r_s = \frac{c_o}{\frac{1}{k_{CO_2}} + \frac{\delta(t)}{D_{O_2}^s} + \frac{1}{k}}$$

$$\left[\frac{1}{k_{CO_2}} + \frac{1}{k} \right] \delta + \frac{1}{2} \frac{\delta^2}{D_{O_2}^s} = c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$

$$r_s = \frac{\rho_{SiO_2}}{M_{SiO_2}} \frac{d\delta}{dt}$$

$$\delta = \varpi_o X_{Si}$$

$$\varpi_o = \frac{\delta_o}{2} \frac{M_{SiO_2}}{M_{Si}} \frac{\rho_{Si}}{\rho_{SiO_2}}$$

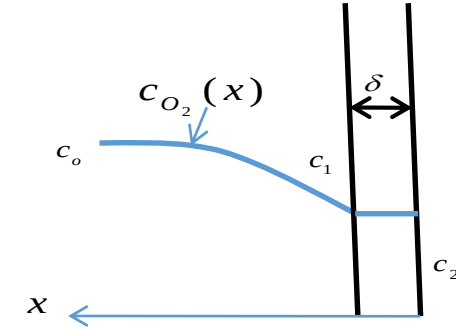
$M_{SiO_2}, M_{Si}, \rho_{SiO_2}, \rho_{Si}$ Molar weights and densities of SiO_2 a Si

δ_o Initial thickness of Si slab

3 limiting cases

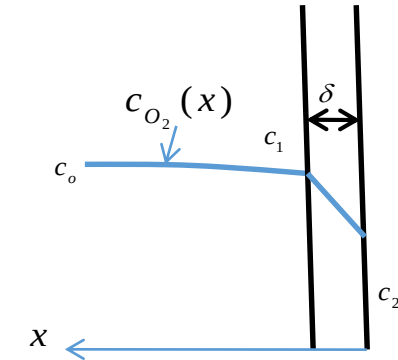
1. Rate determining step is the external mass transfer of oxygen towards interface (gas - SiO₂)

$$\frac{1}{k_{cO_2}} \gg \frac{\delta}{D_{O_2}^s}, \frac{1}{k_{cO_2}} \gg \frac{1}{k} \Rightarrow r_s = k_{cO_2} c_o, \quad \delta = k_{cO_2} c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$



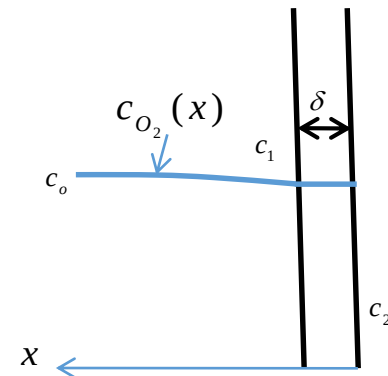
2. Rate determining step is the internal mass transfer of oxygen in porous SiO₂ layer

$$\frac{\delta}{D_{O_2}^s} \gg \frac{1}{k_{cO_2}}, \frac{\delta}{D_{O_2}^s} \gg \frac{1}{k} \Rightarrow r_s = \frac{D_{O_2}^s}{\delta} c_o, \quad \delta = \sqrt{2 D_{O_2}^s c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t}$$



3. Rate determining step is chemical reaction taking place on the interface (SiO₂ - Si)

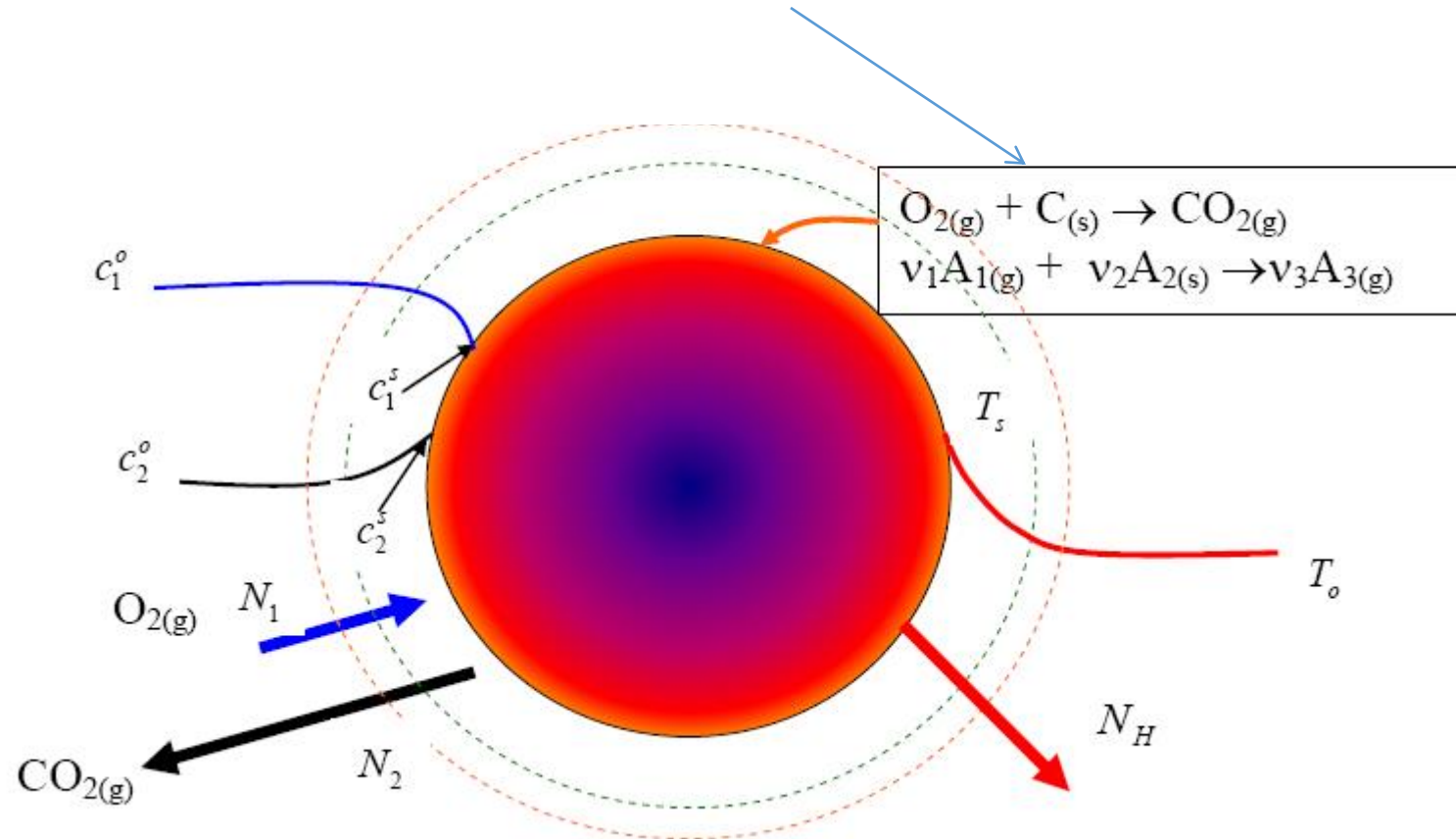
$$\frac{1}{k} \gg \frac{\delta}{D_{O_2}^s}, \frac{1}{k} \gg \frac{1}{k_{cO_2}} \Rightarrow r_s = k c_o, \quad \delta = k c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$



Discussion: $r_s = f(\text{composition})$, $r_s = f(\text{temperature})$

External heat and mass transfer

Combustion of the spherical carbon particle



Conditions in the immediate region of an interface between phases are hard to explore experimentally. In such situations it is helpful to develop a mathematical model of the process starting with the known basic facts. The result of the analysis is then compared with those experimental measurements which it is possible to make. Good agreement suggests that the model may have been realistic.

—T. K. Sherwood, R. L. Pigford, and C. R. Wilke (1975)

Oxygen molar flux at steady state

$$\begin{aligned} N_1 &= k_{c1} a (c_1^o - c_1^s) = -\nu_1 r_V = -(-1) k(T_s) c_1^s = \\ &= A \exp\left(-\frac{E}{RT_s}\right) c_1^s \end{aligned}$$

Energy flux at steady state

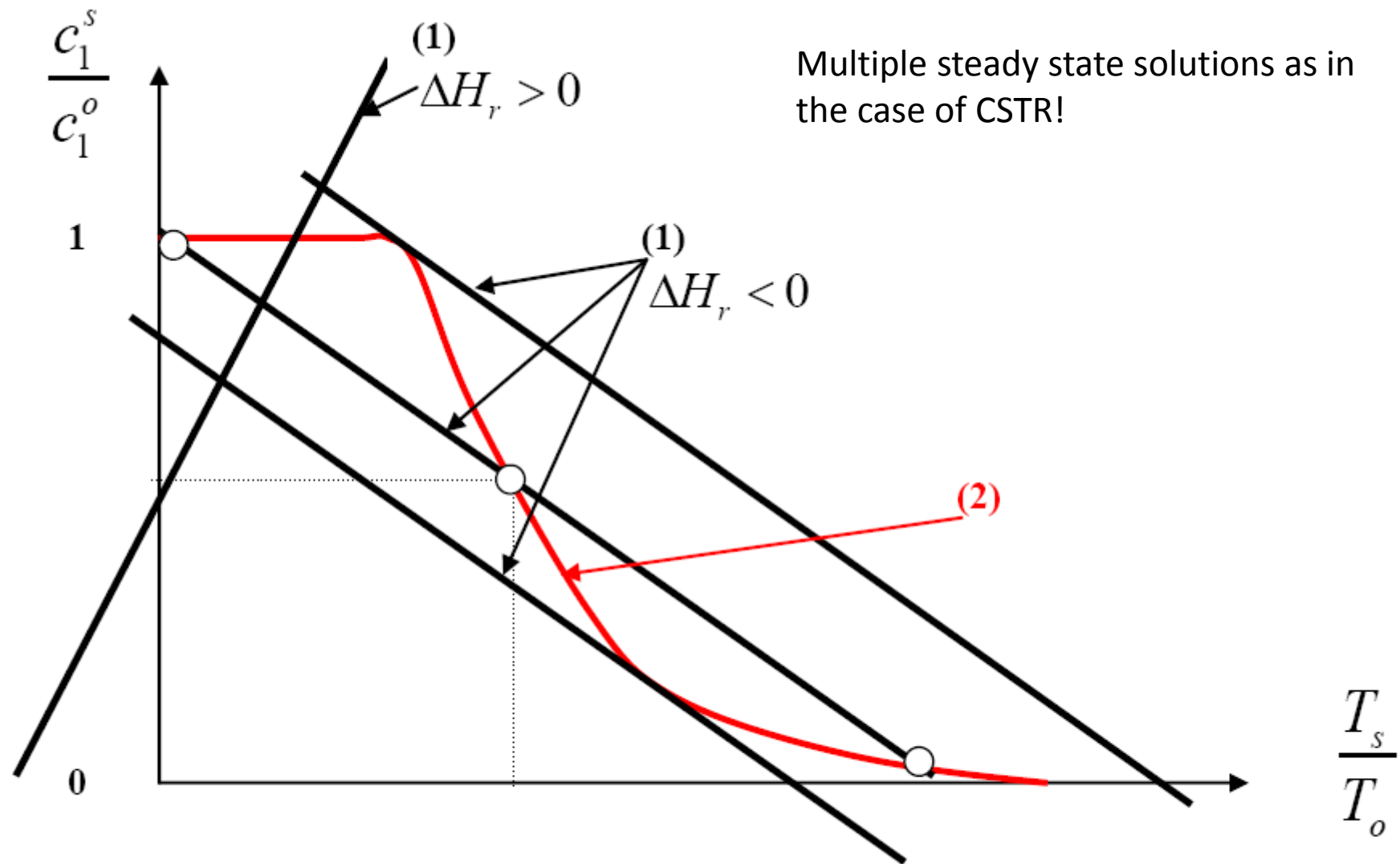
$$N_H = h a (T_s - T_o) = (-\Delta H_r) r_V$$

Surface temperature and concentration of oxygen

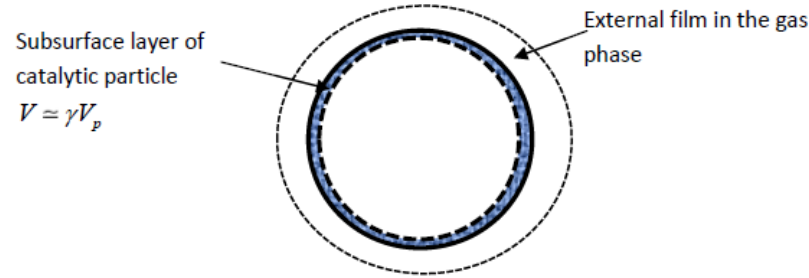
Two balance equations for unknown c_1^s, T_s

$$ha(T_s - T_o) = (-\Delta H_r)r_V = (-\Delta H_r)k_{c1}a(c_1^o - c_1^s)$$
$$\frac{c_1^s}{c_1^o} = 1 - \frac{hT_o}{(-\Delta H_r)k_{c1}c_1^o} \left(\frac{T_s}{T_o} - 1 \right) \quad (1)$$

$$k_{c1}a(c_1^o - c_1^s) = k(T_s)(c_1^s)^n$$
$$n = 1$$
$$\frac{c_1^s}{c_1^o} = \frac{k_{c1}a}{k_{c1}a + k(T_s / T_o)} \quad (2)$$



Example



Molar material balances

$$\varepsilon_p \gamma V_p \frac{dc_i}{dt} = S_e k_{e,i} (c_i^G - c_i^S) + \rho_s (1 - \varepsilon_p) \gamma V_p \sum_{j=1}^{NR} \nu_{ji} r_{M,j}$$

Enthalpy balance

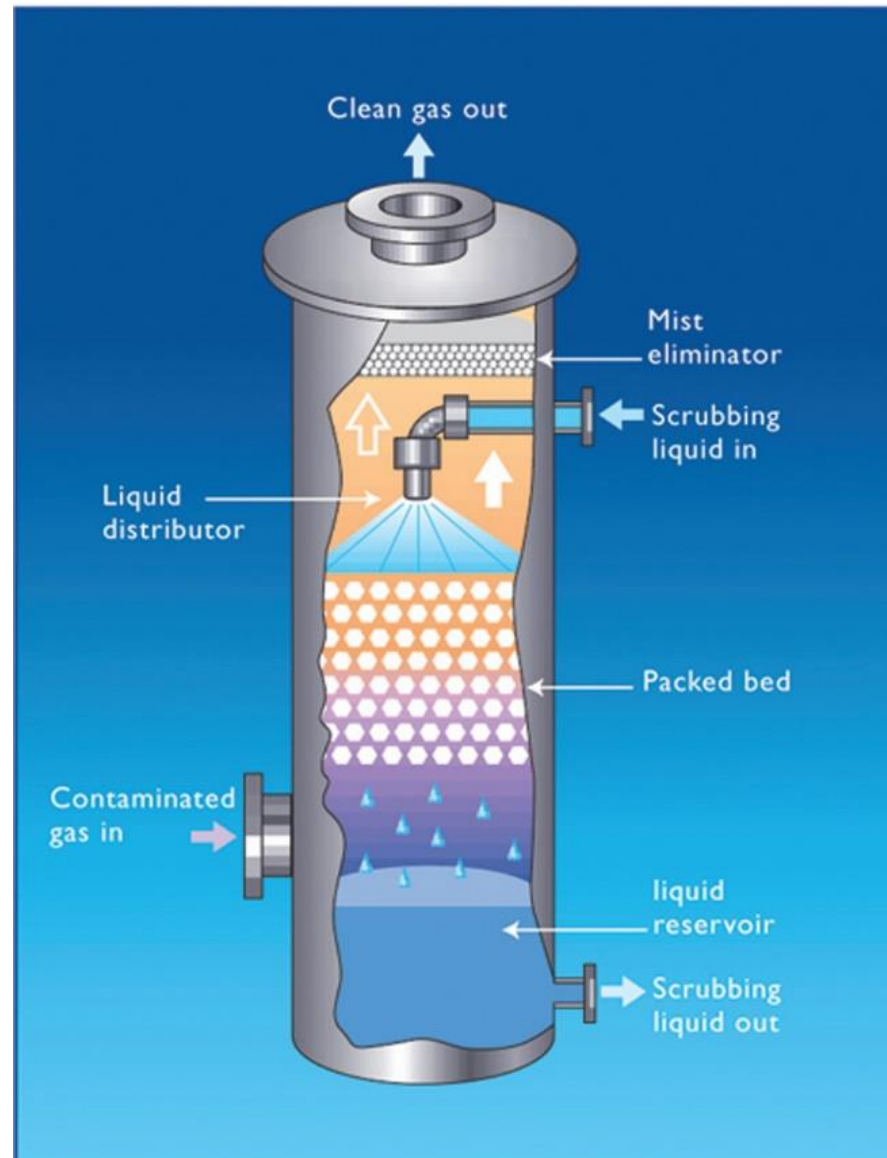
$$\left[(1 - \varepsilon_p) \rho_s V_p c_{pS} + \varepsilon_p V_p \frac{P}{RT_S} c_{pG} \right] \frac{dT_S}{dt} = S_e h (T_G - T_S) + (1 - \varepsilon_p) \gamma \rho_s V_p \sum_{j=1}^{NR} (-\Delta_r H) r_{M,j}$$

$$(1 - \varepsilon_p) \rho_s V_p c_{pS} \frac{dT_S}{dt} = S_e h (T_G - T_S) + (1 - \varepsilon_p) \gamma \rho_s V_p \sum_{j=1}^{NR} (-\Delta_r H) r_{M,j}$$

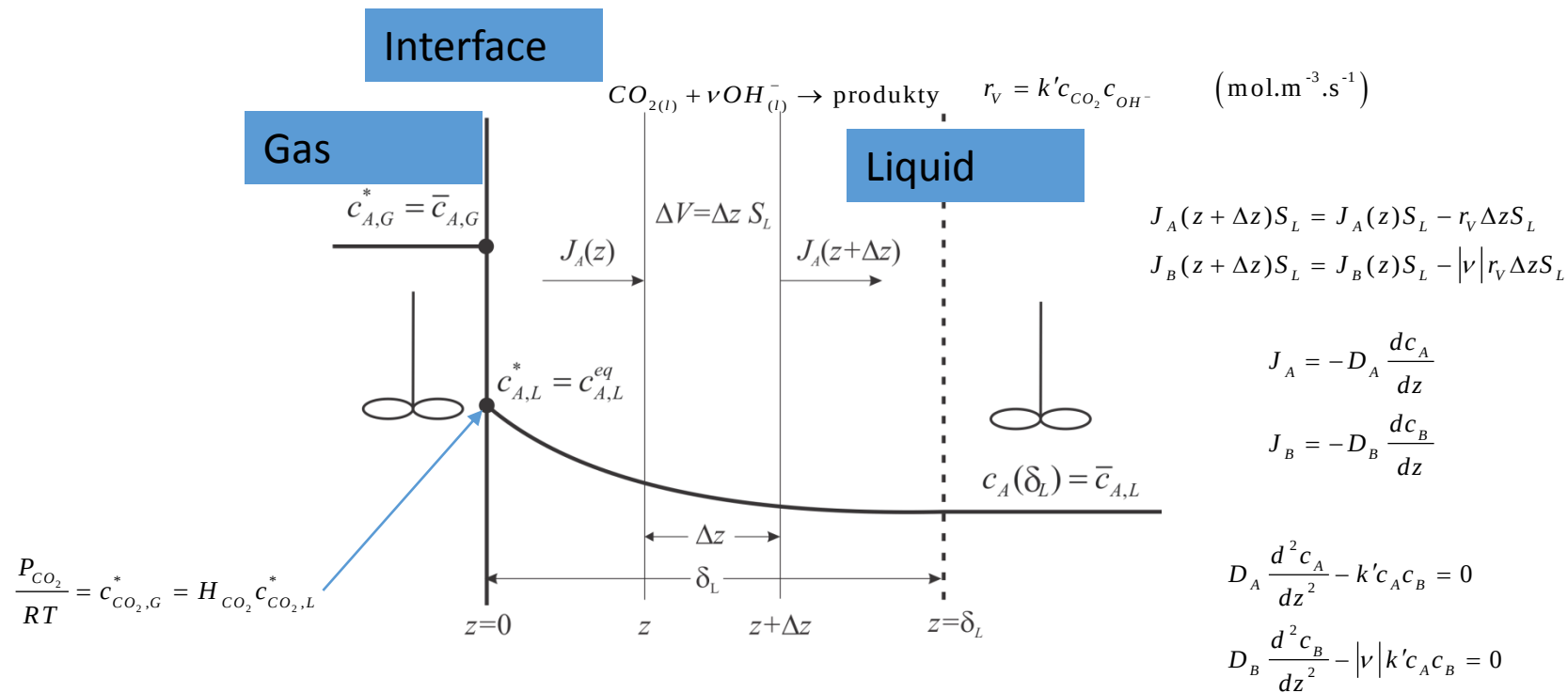
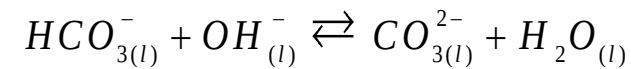
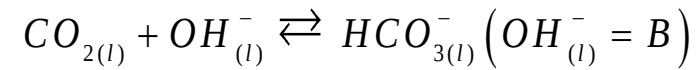
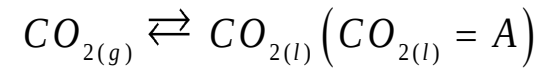


$r_{M,1} = A_1 \exp\left(-\frac{E_1}{RT}\right) P_{s,\text{NH}_3} P_{s,\text{O}_2} \quad \text{mol.kg}^{-1}.\text{s}^{-1}$	$A_1 = 4.609 \times 10^{+3} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_1 = 149.1 \text{ kJ.mol}^{-1}$	(1)
$r_{M,2} = A_2 \exp\left(-\frac{E_2}{RT}\right) P_{s,\text{NH}_3} P_{s,\text{O}_2} \quad \text{mol.kg}^{-1}.\text{s}^{-1}$	$A_2 = 5.0 \times 10^{-2} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_2 = 61.0 \text{ kJ.mol}^{-1}$	(2)
$r_{M,3} = A_3 \exp\left(-\frac{E_3}{RT}\right) P_{s,\text{NH}_3} P_{s,\text{O}_2} \quad \text{mol.kg}^{-1}.\text{s}^{-1}$	$A_3 = 2.8 \times 10^{-2} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_3 = 104.0 \text{ kJ.mol}^{-1}$	(3)

Heterogeneous gas-liquid reactions



Kinetics of gas-liquid reactions



$$D_A \frac{d^2 c_A}{dz^2} - k' c_A c_B = 0$$

$$D_B \frac{d^2 c_B}{dz^2} - |\nu| k' c_A c_B = 0$$

Boundary conditions

$$z = 0 : c_A = c_{A,L}^{eq}, \frac{dc_B}{dz} = 0 \quad \text{or} \quad z = 0; -D_A \frac{dc_A}{dz} = k_{cA,G} (\bar{c}_{A,G} - c_{A,G}^*) = k_{cA,G} (\bar{c}_{A,G} - H_A c_A(z=0)), \frac{dc_B}{dz} = 0$$

$$z = \delta_L : -S_L D_A \frac{dc_A}{dz} = k' c_A \bar{c}_{B,L} (V_L - S_L \delta_L), c_B = \bar{c}_{B,L}$$

Dimensionless form

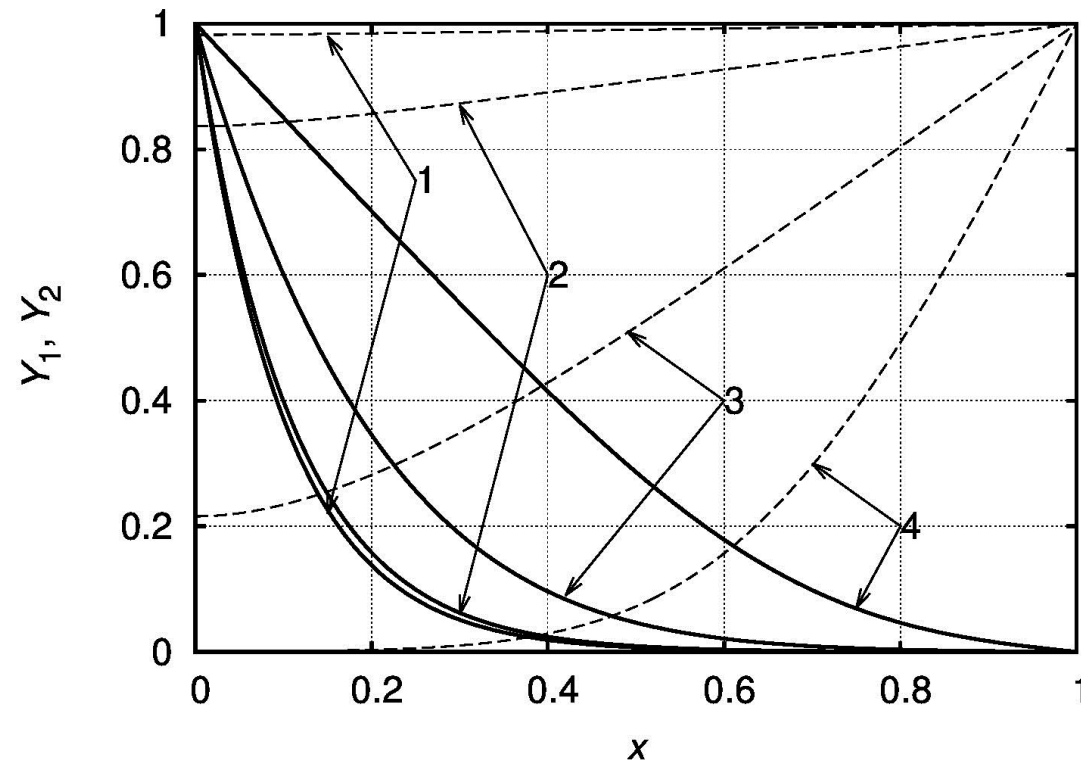
$$x = \frac{z}{\delta_L}, Y_1 = \frac{c_{CO_2}}{c_{CO_2,L}^{eq}} = \frac{c_A}{c_{A,L}^{eq}}, Y_2 = \frac{c_{OH^-}}{\bar{c}_{OH^-,L}} = \frac{c_B}{\bar{c}_{B,L}}$$

$$\frac{d^2 Y_1}{dx^2} - \text{Ha}^2 Y_1 Y_2 = 0 \quad \frac{d^2 Y_2}{dx^2} - \chi \text{Ha}^2 Y_1 Y_2 = 0$$

$$x = 0; \quad Y_1 = 1, \frac{dY_2}{dx} = 0 \quad x = 1; \quad -\frac{dY_1}{dx} = \text{Ha}^2 Y_1 \left(\frac{V_L}{S_L \delta_L} - 1 \right), Y_2 = 1$$

$$\text{Ha} = \frac{\sqrt{k' \bar{c}_B D_A}}{D_A / \delta_L} = \frac{\sqrt{k' \bar{c}_B D_A}}{k_{A,L}^o} \quad \chi = |\nu| \frac{D_A c_{A,L}^{eq}}{D_B \bar{c}_{B,L}} \quad k_{A,L}^o = D_A / \delta_L$$

Numerical solution gives to us concentration profiles

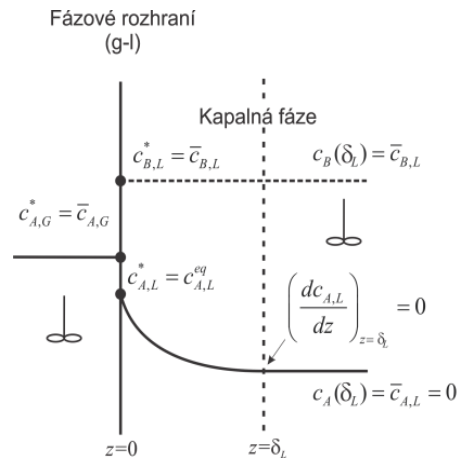


We get the overall rate of CO₂ absorption by integration of local rate

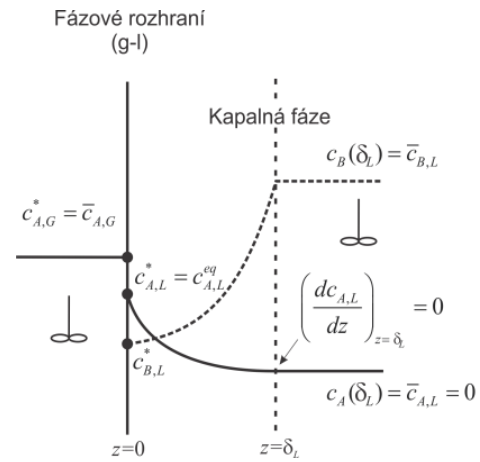
$$R_A = -\frac{1}{V_L} \int_0^{V_L} r_V dV \quad - \left[-S_L D_A \left(\frac{dc_A}{dz} \right)_{z=0} \right] = V_L R_A \quad \frac{S_L D_A c_{A,L}^{eq}}{V_L \delta_L} \left(\frac{dY_1}{dx} \right)_{x=0} = R_A$$

Limiting situations

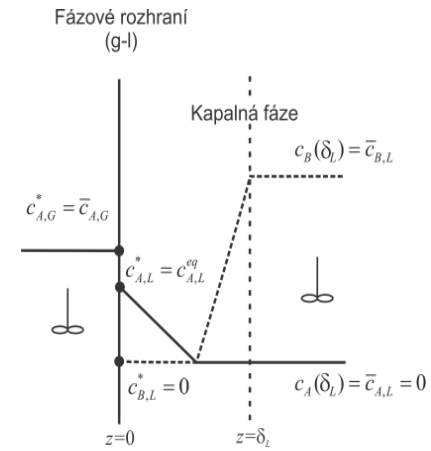
$$\chi = \left| \nu \right| \frac{D_A}{D_B} \frac{c_{A,L}^{eq}}{\bar{c}_{B,L}} < 10^{-3}$$



$$\chi = \left| \nu \right| \frac{D_A}{D_B} \frac{c_{A,L}^{eq}}{\bar{c}_{B,L}} > 10^{-2}$$



$$Ha > 3$$





9. Kinetics of catalytic reactions

• homogeneous catalysis

- Ozone decomposition in the presence of Cl
- SO₂ oxidation by NO_x
- Esterification catalyzed by acids or bases
- Enzymatic catalysis

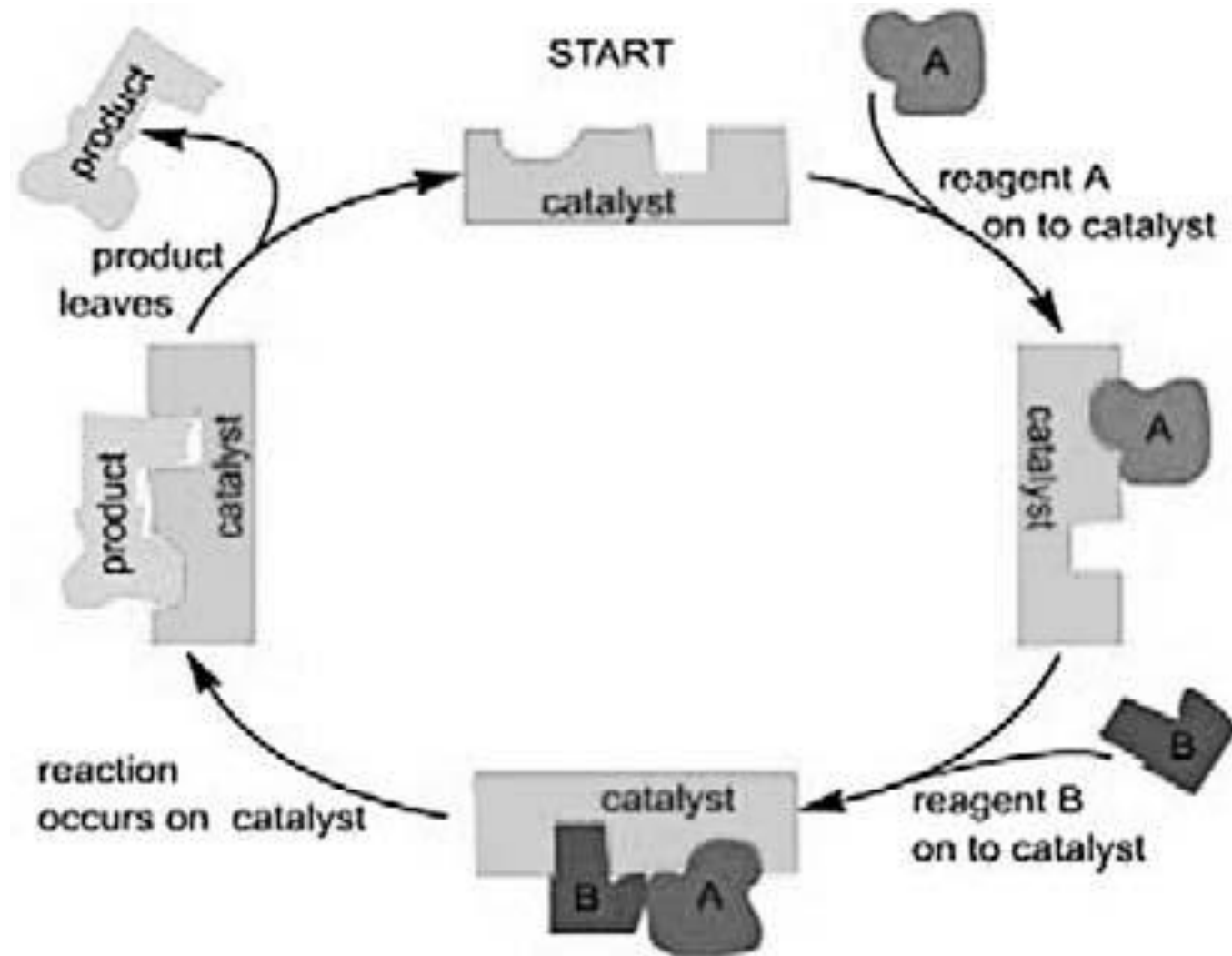


• heterogeneous catalysis

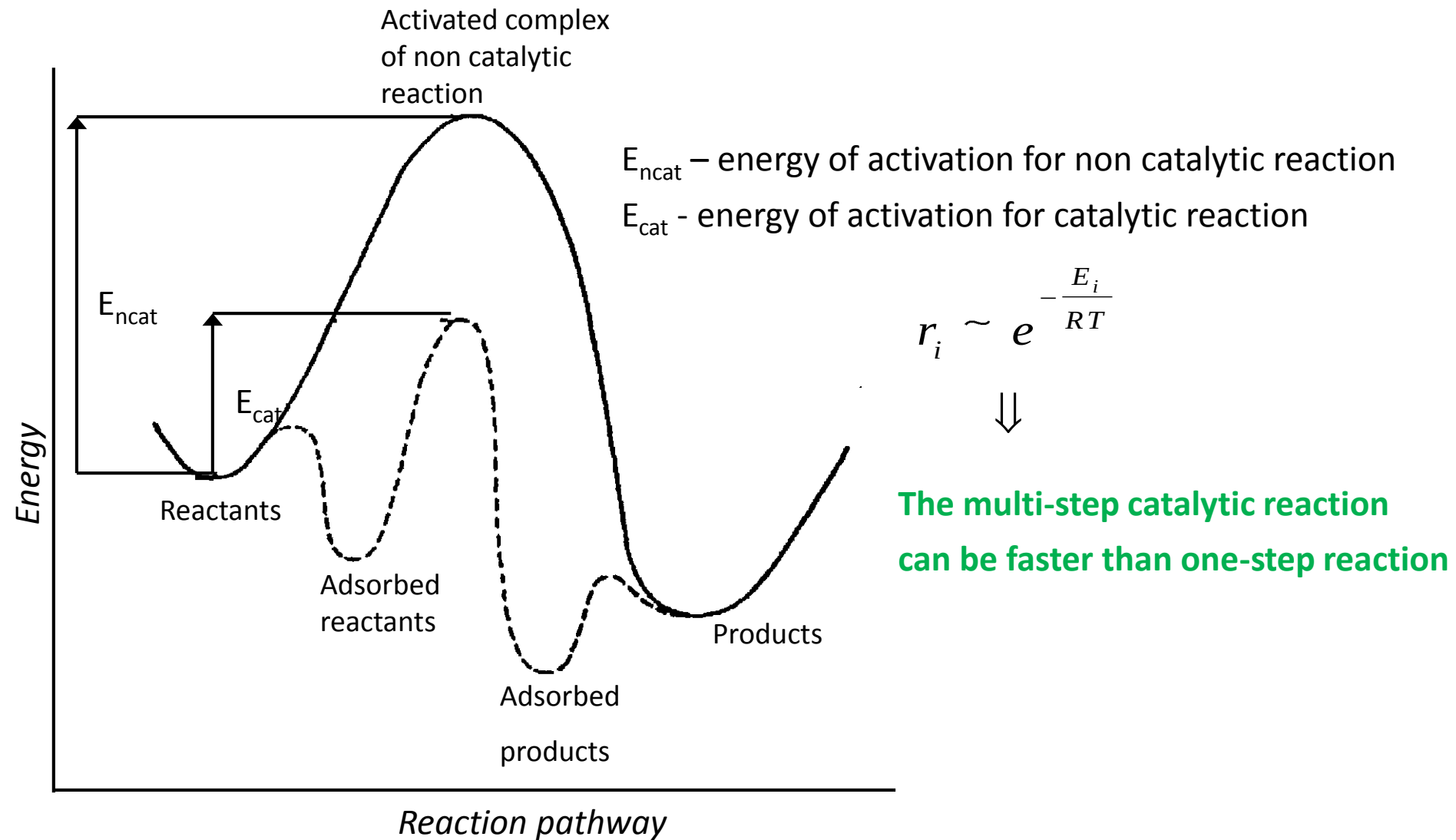
- NH₃, CH₃OH production
- SO₂ to SO₃ oxidation
- HDS, HDN processes
- Fluid Catalytic Cracking
- Hydrogenation
- Polymerization (Ziegler-Natta catalysts, metallocens)



Catalytic cycle



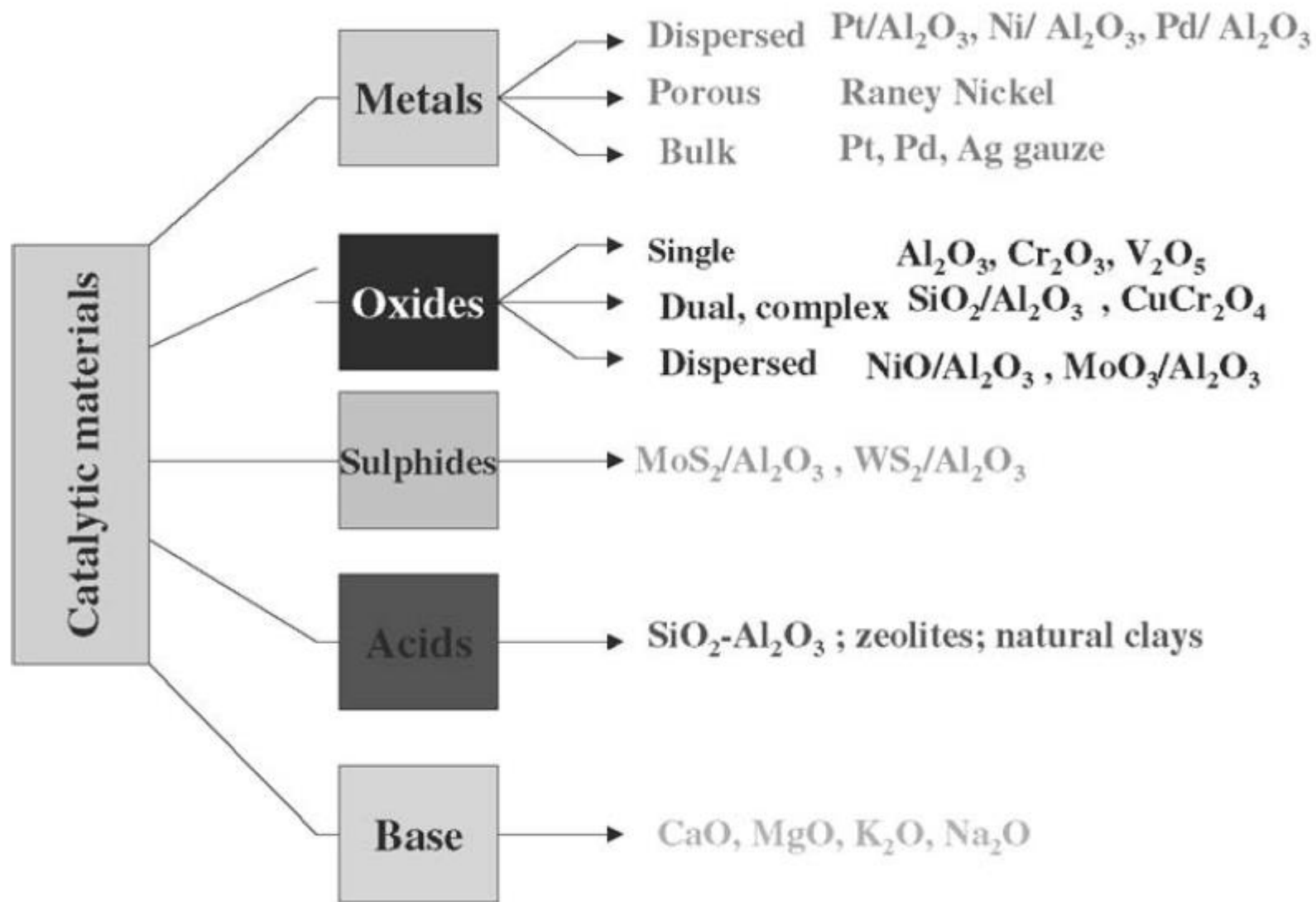
Non catalytic x catalytic reaction



Homogeneous x Heterogeneous Catalysts

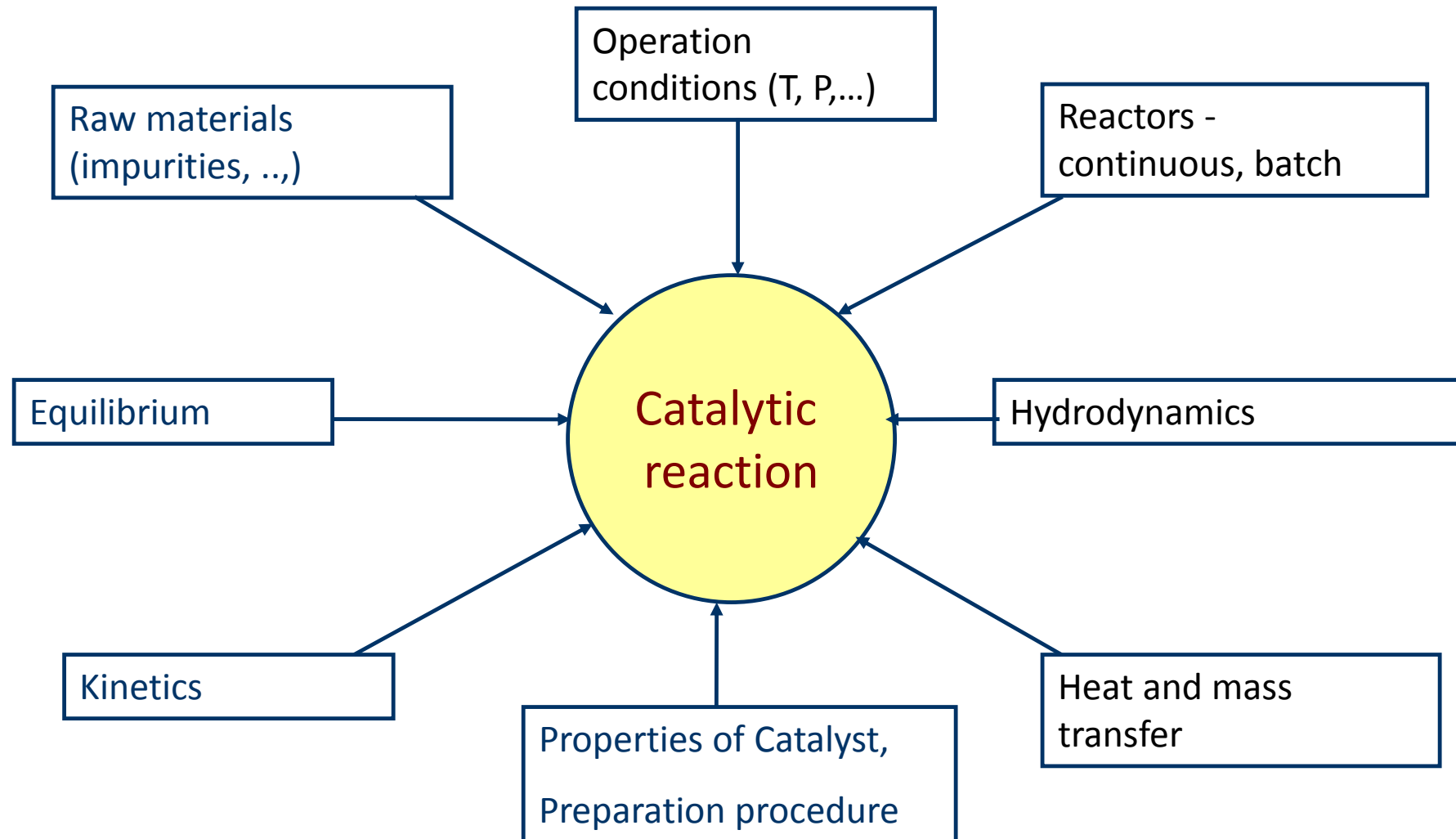
		Homogeneous	Heterogeneous
Active sites	Concentration	All atoms	Surface atoms
	Diffusion disguises	No	Important
	Reaction conditions	50-200 °C	200-1000 °C
	Application	Limited	Large
Characterization	Structure, composition	Well defined	No clear definition
	Modification	Easy	Difficult
	Temperature stability	Low	High
Separation		Difficult	Easy
			packed beds
Recycling		Feasible	Feasible

Reactant(s)	Product	Typical catalyst(s)	Global Production/t year ⁻¹
Crude oil	Hydrocarbon fuels	Platinum/silica-alumina Platinum/acidic alumina Metal-exchanged zeolites	1*10 ⁹
SO ₂ , O ₂	Sulphuric acid	V ₂ O ₅	1.4*10 ⁸
N ₂ , H ₂	Ammonia	Fe	9*10 ⁷
NH ₃ , O ₂	Nitric acid	Pt/Rh	2.5* 10 ⁷
CO, H ₂	Methanol	Cu/ZnO	1.5*10 ⁷
C ₂ H ₄ , O ₂	Ethylene oxide	Ag	1*10 ⁷
Unsaturated vegetable oils, H ₂	Hydrogenated vegetable oils	Ni	8*10 ⁶
C ₂ H ₄	Polyethylene	Cr(II), Ti(III)	6*10 ⁶
CH ₃ OH, O ₂	Formaldehyde	Mixed Fe, Mo oxides	5*10 ⁶
C ₃ H ₆ , NH ₃ , O ₂	Acrylonitrile	Mixed Bi, Mo oxides	3*10 ⁶
o -Xylene, O ₂	Phthalic anhydride	V ₂ O ₅	4*10 ⁶
n-Butane, O ₂	Maleic anhydride	V ₂ O ₅	4*10 ⁵



Catalyst	Reaction
Metals (e.g., Ni, Pd, Pt, as powders or on supports) or metal oxides (e.g., Cr ₂ O ₃)	C=C bond hydrogenation, e.g., olefin + H ₂ → paraffin
Metals (e.g., Cu, Ni, Pt)	C=O bond hydrogenation, e.g., acetone + H ₂ → isopropanol
Metal (e.g., Pd, Pt)	Complete oxidation of hydrocarbons, oxidation of CO
Fe (supported and promoted with alkali metals)	3H ₂ + N ₂ → 2NH ₃
Ni	CO + 3H ₂ → CH ₄ + H ₂ O (methanation)
Fe or Co (supported and promoted with alkali metals)	CO + H ₂ → paraffins + olefins + H ₂ O + CO ₂ (+ other oxygen-containing organic compounds) (Fischer-Tropsch reaction)
Cu (supported on ZnO, with other components, e.g., Al ₂ O ₃)	CO + 2H ₂ → CH ₃ OH
Re + Pt (supported on η-Al ₂ O ₃ or γ-Al ₂ O ₃ promoted with chloride)	Paraffin dehydrogenation, isomerization and dehydrocyclization

Catalyst	Reaction
Solid acids (e.g., $\text{SiO}_2\text{-Al}_2\text{O}_3$, zeolites)	Paraffin cracking and isomerization
$\gamma\text{-Al}_2\text{O}_3$	Alcohol $\rightarrow$ olefin + H_2O
Pd supported on acidic zeolite	Paraffin hydrocracking
Metal-oxide-supported complexes of Cr, Ti or Zr	Olefin polymerization, e.g., ethylene $\rightarrow$ polyethylene
Metal-oxide-supported oxides of W or Re	Olefin metathesis, e.g., 2 propylene $\rightarrow$ ethylene + butene
Ag(on inert support, promoted by alkali metals)	Ethylene + $1/2 \text{O}_2 \rightarrow$ ethylene oxide (with $\text{CO}_2 + \text{H}_2\text{O}$)
V_2O_5 or Pt	$2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$
V_2O_5 (on metal oxide support)	Naphthalene + $9/2 \text{O}_2 \rightarrow$ phthalic anhydride + $2\text{CO}_2 + 2\text{H}_2\text{O}$
Bismuth molybdate	Propylene + $1/2 \text{O}_2 \rightarrow$ acrolein
Mixed oxides of Fe and Mo	$\text{CH}_3\text{OH} + \text{O}_2 \rightarrow$ formaldehyde (with $\text{CO}_2 + \text{H}_2\text{O}$)
Fe_3O_4 or metal sulfides	$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$

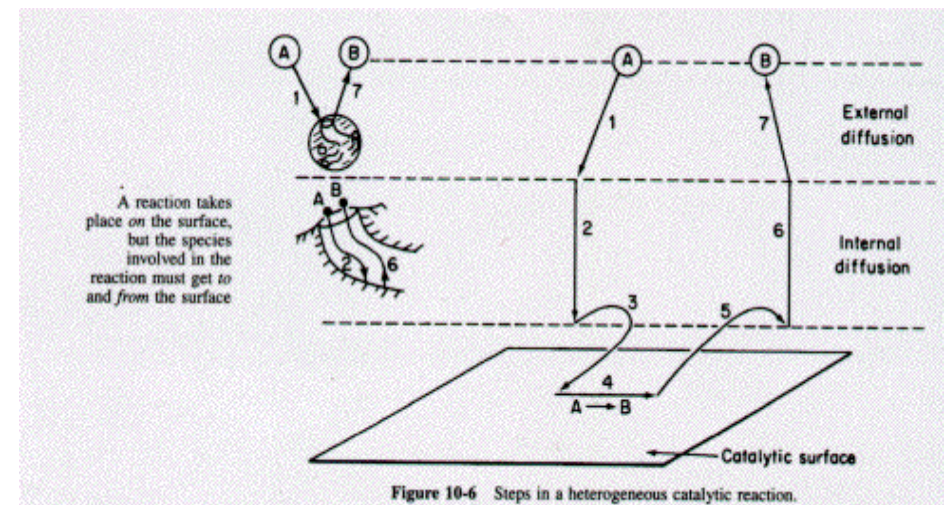


Steps in a catalytic reaction

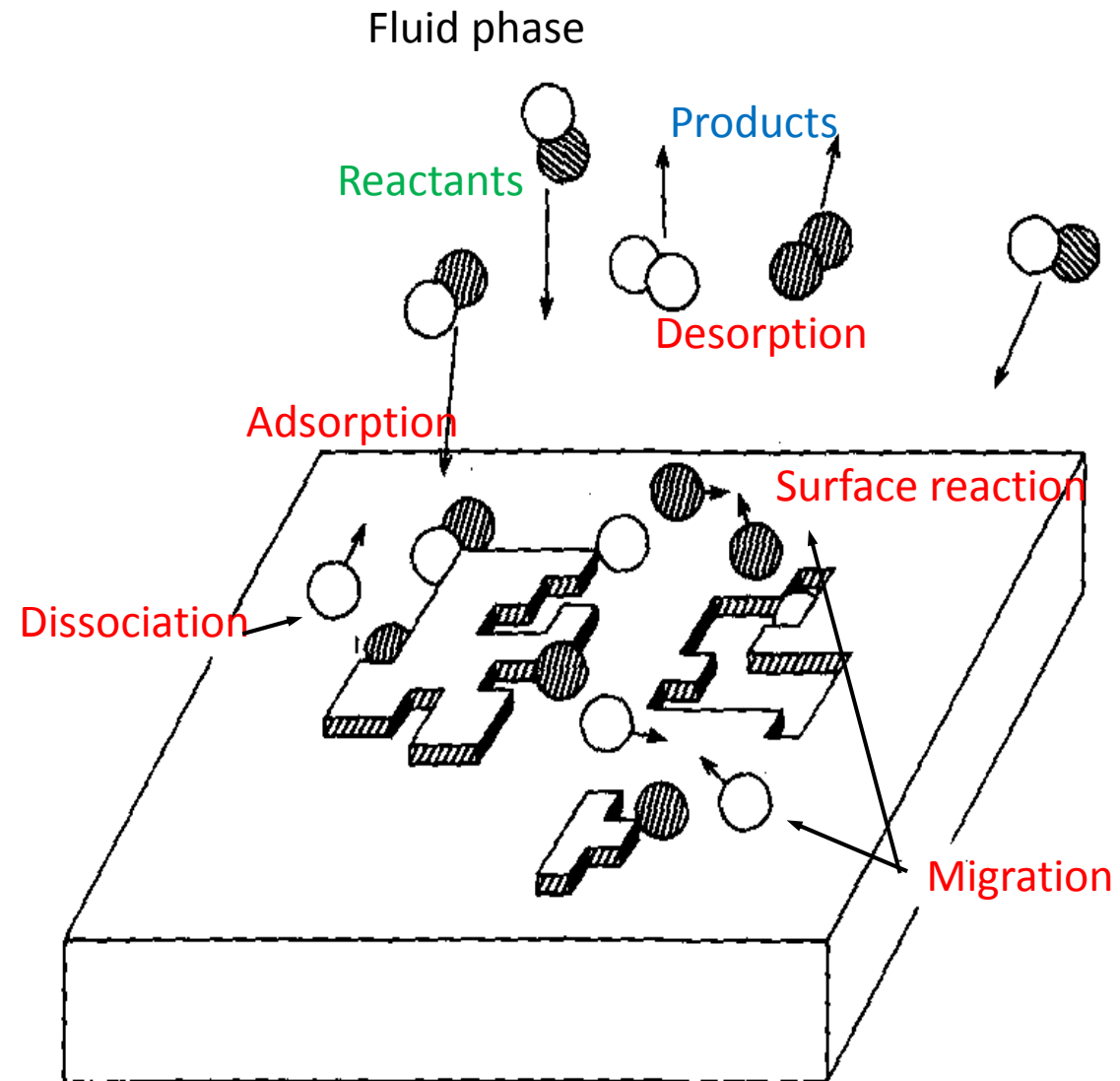
- 1) Mass transfer of reactants to the external surface of catalyst
- 2) Mass transfer of reactants in porous structure of catalyst
- 3) *Adsorption of reactants*
- 4) *Surface reaction (+ migration)*
- 5) *Desorption of products*
- 6) Mass transfer of products in porous structure of catalyst
- 7) Mass transfer of reactants from the external surface of catalyst

The transport steps (1,2,6,7) depend on T, P, composition, flow rates, pore size,

The chemical steps (3,4,5) are dependent on T, P, composition.



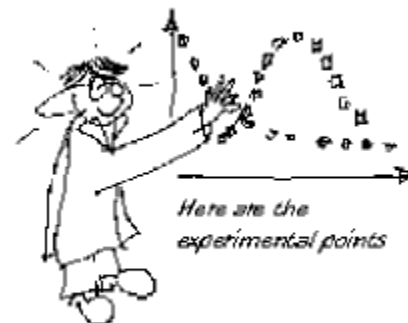
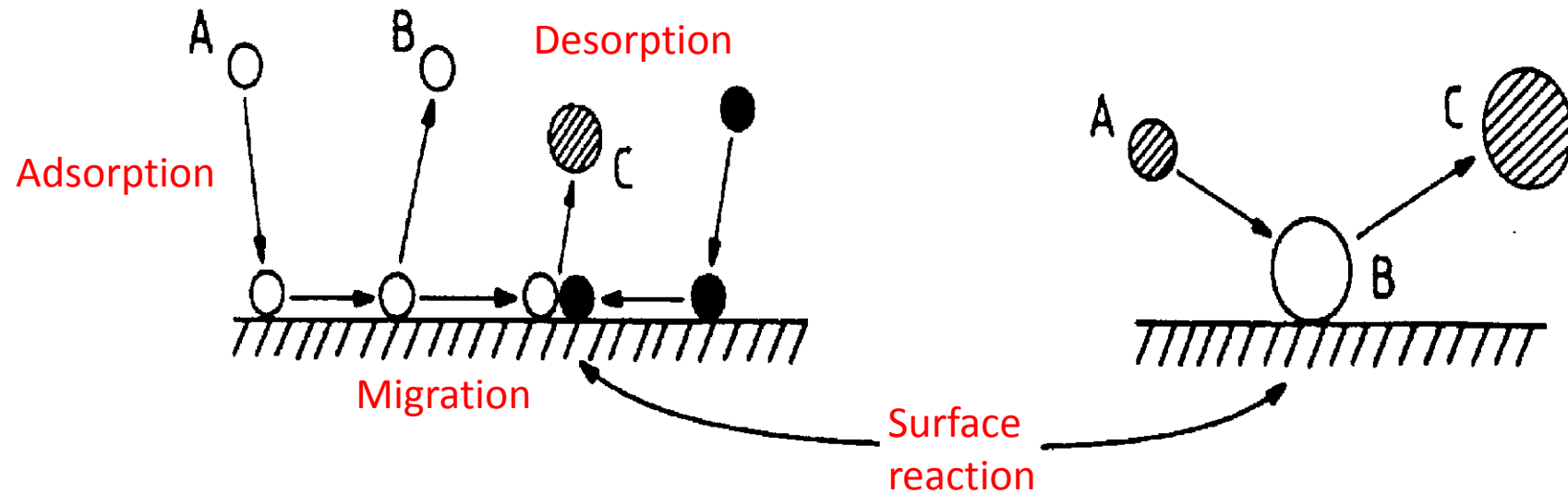
Elementary steps of catalytic reaction



Mechanisms in heterogeneous catalysis

Langmuir-Hinshelwood

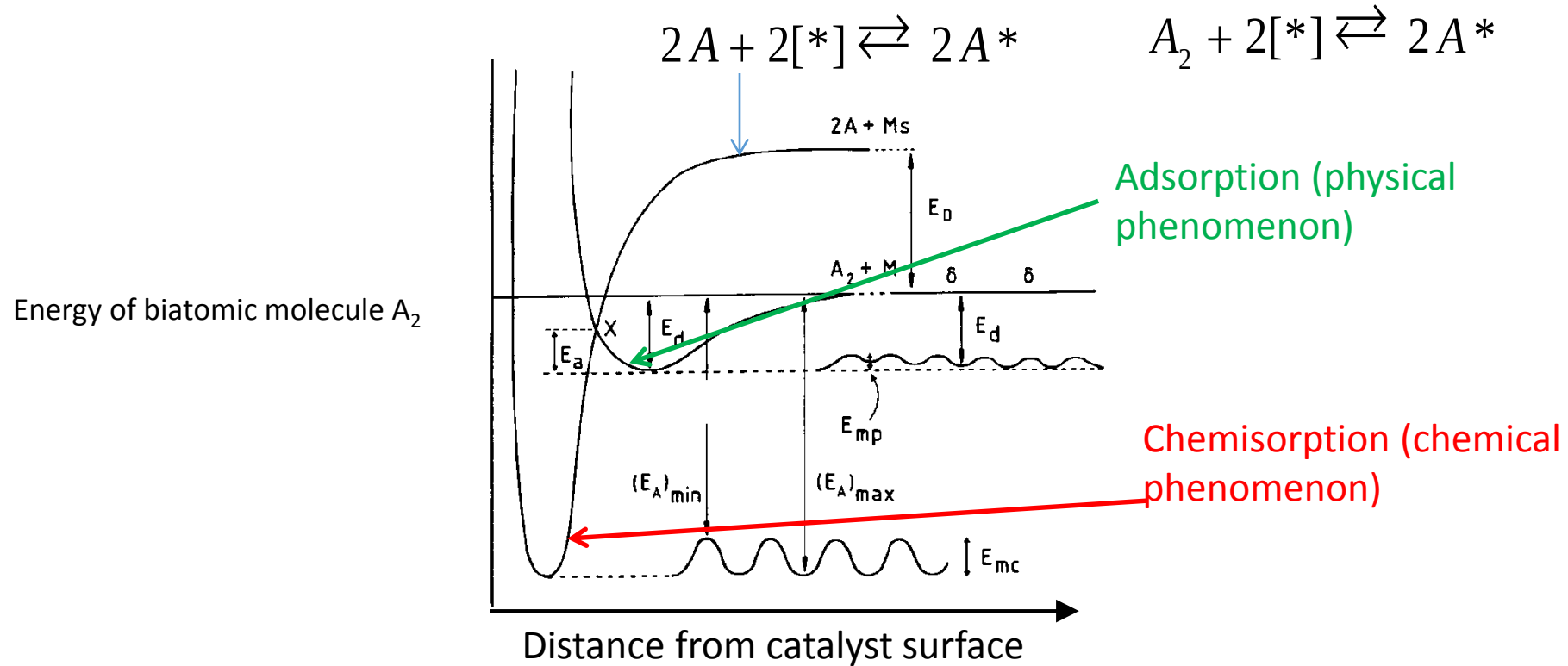
Rideal-Eley



Here is the kinetic model

$$r = \frac{k_f A B}{(1 + K_A A + K_B B)^2}$$

Adsorption x Chemisorption

 E_{mc}, E_{mp} – activation energy of migration in adsorbed and chemisorbed state

E_D – energy of dissociation of molecule A_2

E_d – energy of desorption of A_2

E_a – energy of activation of transition from adsorbed to chemisorbed state

Adsorption x Chemisorption

	<i>Adsorption</i>	<i>Chemisorption</i>
Principal	van der Waals forces no electron transfer !	covalent or ionic bonds electron transfer
Adsorbent	all solids	specific sites
Adsorbat	gases $T < T_c$	reactive components
Temperature	low	higher
Enthalpy	10-40 kJ/mol	80-600 kJ/mol
Rate	high	depends on T
Activation energy	low	high
Occupancy	multilayer	monolayer
Reversibility	YES	YES but ...
Use	BET method pore size distribution	surface concentration of active sites

Chemisorption of fluid phase molecule (adsorbat)

Surface occupancy(Θ)

$$\Theta_i = \frac{\text{Number of sites occupied by i-th component}}{\text{Total number of sites}}$$

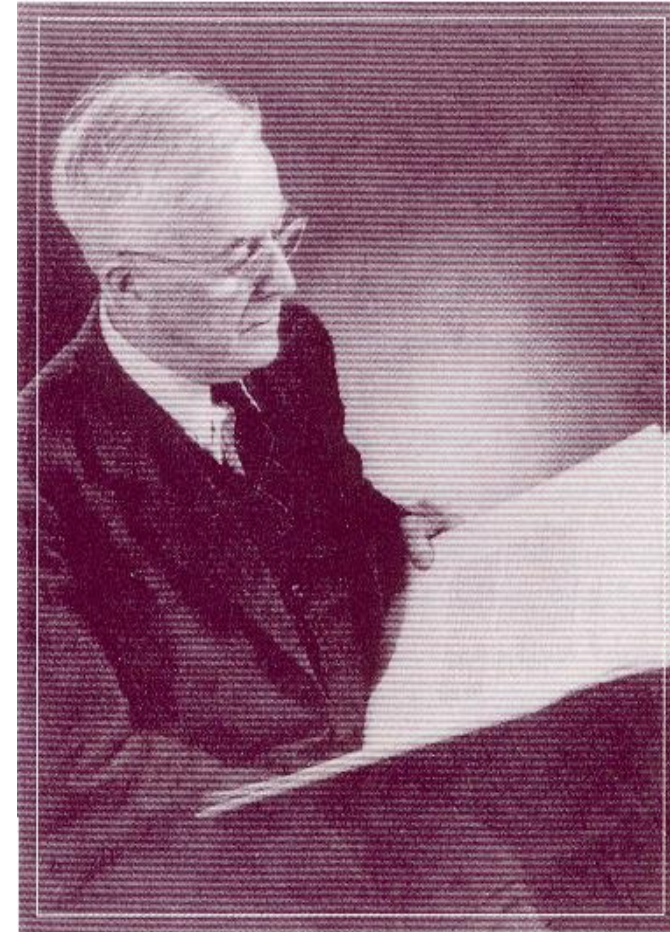
$$0 < \Theta_i < 1$$

Associative x Dissociative chemisorption

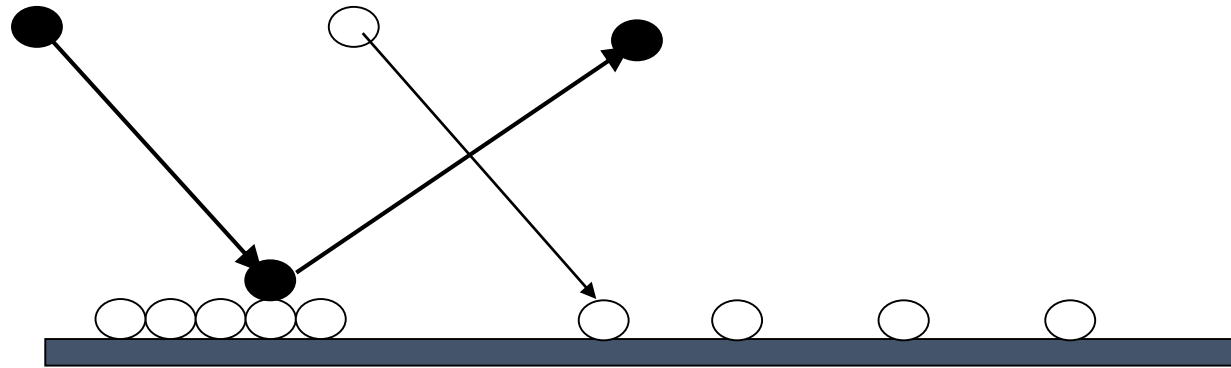
Adsorption (chemisorption) isotherm – Surface occupancy as a function of partial pressure of given component at constant temperature

Irving Langmuir

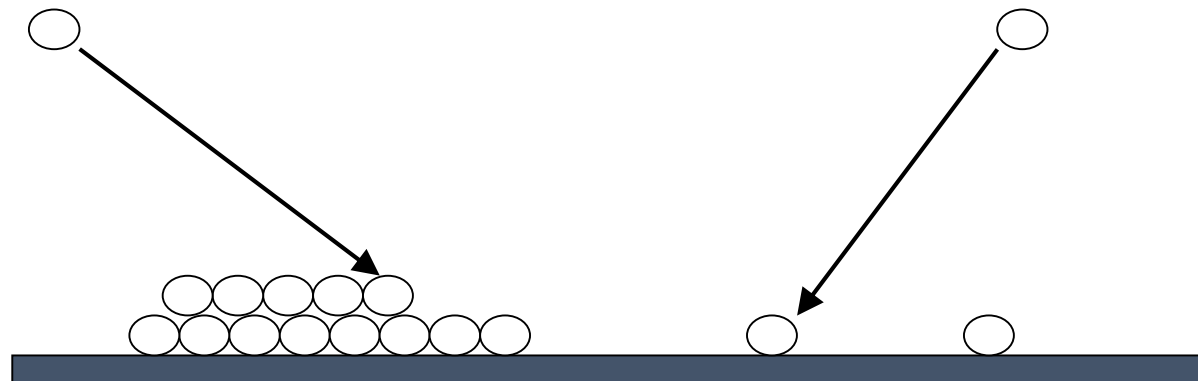
- 1920
 - adsorption isotherm
 - kinetics of catalytic reactions on ideal surfaces
- 1932
 - Nobel Prize



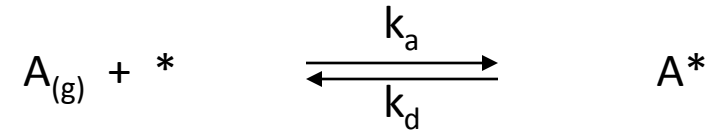
Langmuir adsorption isotherm



Brunauer-Emmett-Teller (BET) adsorption isotherm



Associative adsorption on ideal catalytic surface



$$\text{Rate of chemisorption} = k_a \cdot P_A \cdot (1 - \Theta_A)$$

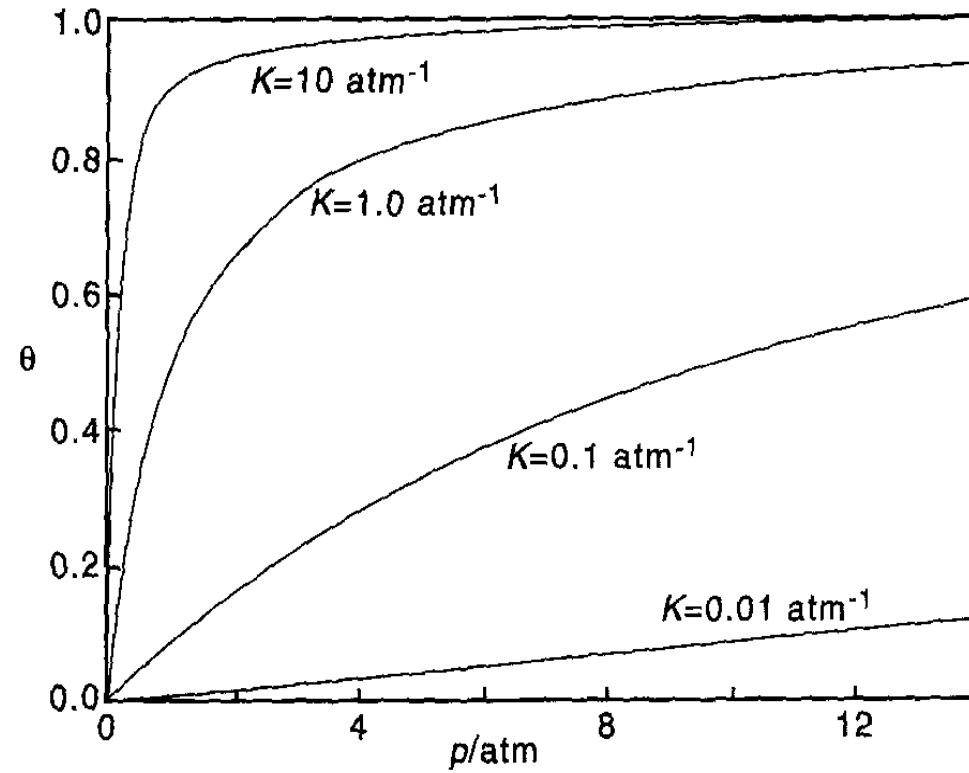
$$\text{Rate of desorption} = k_d \cdot \Theta_A$$

At equilibrium

$$k_a \cdot p \cdot (1 - \Theta_A) = k_d \cdot \Theta_A \quad (K_A = k_a/k_d)$$

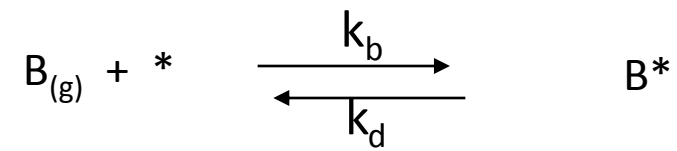
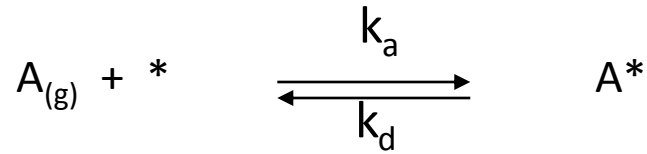
$$\frac{\Theta_A}{(1 - \Theta_A)} = K_A \cdot P_A \quad \Rightarrow \quad \Theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

Associative chemisorption



Langmuir adsorption (chemisorption) isotherm

Multicomponent associative chemisorption on ideal catalytic surface



Occupancy of A

$$\Theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

Occupancy of B

$$\Theta_B = \frac{K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

$$K_A = k_a / k_d$$

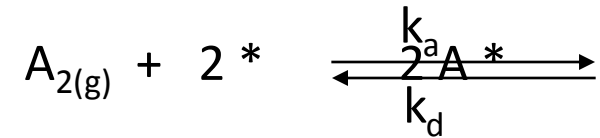
$$K_B = k_b / k_d$$

Irreversible chemisorption



catalyst poisoning

Dissociative chemisorption on ideal catalytic surface



$$\text{Rate of chemisorption} = k_a \cdot P_A \cdot (1 - \Theta_A)^2$$

$$\text{Rate of desorption} = k_d \cdot \Theta_A^2$$

At equilibrium

$$k_a \cdot p \cdot (1 - \Theta_A)^2 = k_d \cdot \Theta_A^2 \quad (K_A = k_a/k_d)$$

$$\frac{\Theta_A^2}{(1 - \Theta_A)^2} = K_A \cdot P_A \quad \Rightarrow \quad \Theta_A = \frac{\sqrt{K_A P_A}}{1 + \sqrt{K_A P_A}}$$

Isotherms

Langmuir

(chemisorption, adsorption,
monolayer, micropores)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = \frac{K_A P_A}{1 + K_A P_A}$$

Henry

(chemisorption, adsorption, low occupancy)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = K_A P_A$$

Freundlich

(chemisorption, adsorption, non ideal)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = K_A (P_A)^{\frac{1}{n}}$$

Temkin

(chemisorption, non ideal)

$$\frac{(n_A)_{adsorbed}}{(n_*)} = \Theta_A = \alpha_A \ln(\beta_A P_A)$$

Brunauer-Emmett-Teller (BET)

(adsorption, multilayer)

$$\frac{P_A}{(n_A)_{ads} (P_A^o - P_A)} = \frac{1}{n_m C} + \frac{(C-1)}{n_m C} \frac{P_A}{P_A^o}$$

Virial

(adsorption, multilayer)

$$\frac{P_A}{R.T} = \Theta_A (1 + a_1 \Theta_A + a_2 \Theta_A^2 + \dots)$$

Brunauer-Emmett-Teller (BET)

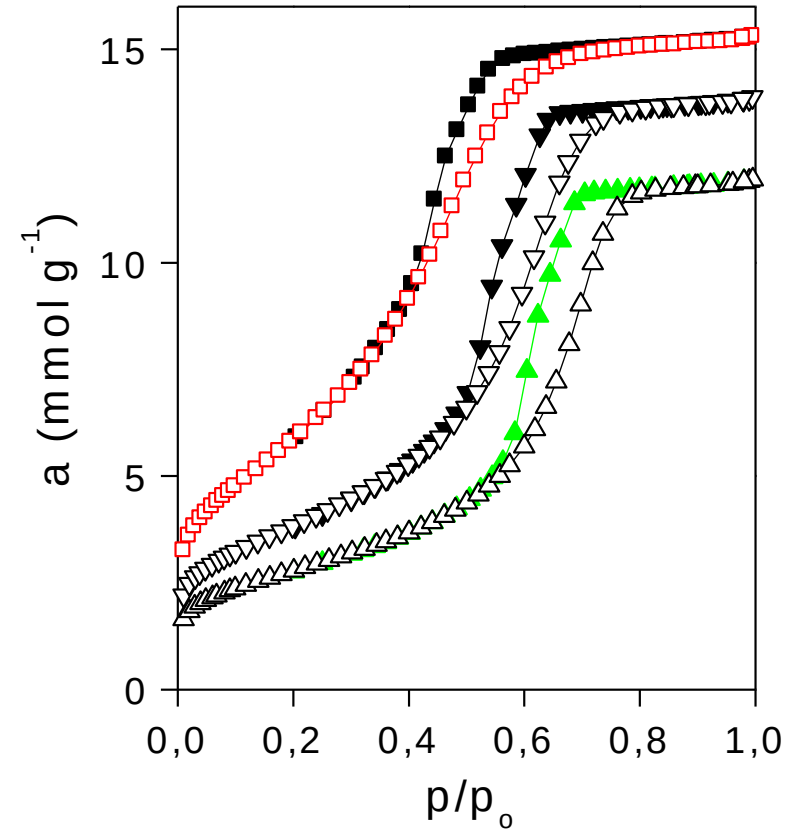
Extention of Langmuir model

Assumptions:

- adsorption in multilayer s, 1st layer interaction between adsorbent and adsorbate, in 2nd and further layers condensation-like interaction

$$\frac{P_A}{(n_A)_{ads} (P_A^o - P_A)} = \frac{1}{n_m C} + \frac{(C - 1) P_A}{n_m C P_A^o}$$

Mesoporous alumina



Temperature of calcination : 3,3 nm (450 °C) - 4,5 nm (600 °C) - 5,1 nm (800 °C)

Reaction rate per mass

$$r_M = \frac{1}{m} r = \frac{1}{m} \frac{d\xi}{dt} = \frac{1}{m} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.kg}^{-1}.\text{s}^{-1}$$

$$r_{M,k} = \frac{1}{m} r_k = \frac{1}{m} \frac{d\xi_k}{dt}$$

Reaction rate per surface

$$r_S = \frac{1}{S} r = \frac{1}{S} \frac{d\xi}{dt} = \frac{1}{S} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.m}^{-2}.\text{s}^{-1}$$

$$r_{S,k} = \frac{1}{S} r_k = \frac{1}{S} \frac{d\xi_k}{dt}$$

Reaction rate per active center (turnover number)

$$r_{RS} = \frac{1}{n_{RS}} r = \frac{1}{n_{RS}} \frac{d\xi}{dt} = \frac{1}{n_{RS}} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{s}^{-1}$$

$$r_{RS,k} = \frac{1}{n_{RS}} r_k = \frac{1}{n_{RS}} \frac{d\xi_k}{dt}$$

Reaction rate of catalytic reactions

Langmuir-Hishelwood ideal surface

- ⊙ Rate of elementary steps
- ⊙ Rate determining step x steady state hypothesis

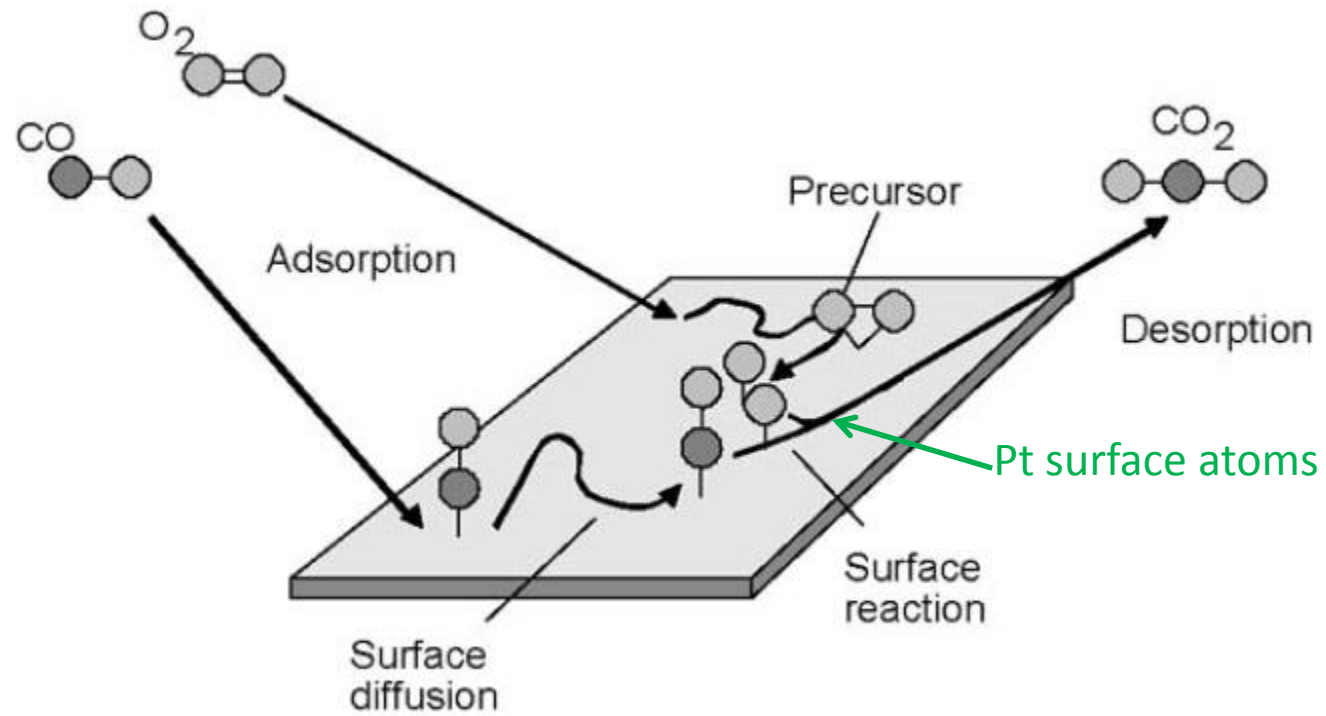
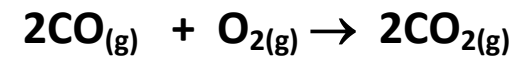
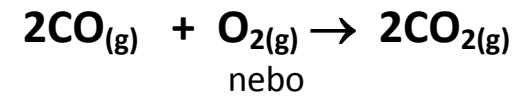
Reaction rate of catalytic reactions

Langmuir-Hishelwood ideal surface

- ⊙ Rate of elementary steps
- ⊙ Rate determining step x steady state hypothesis

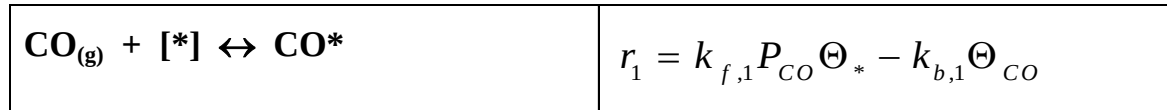
CO oxidation on Pt

Overall reaction ($\Delta G_r^\circ < 0$)



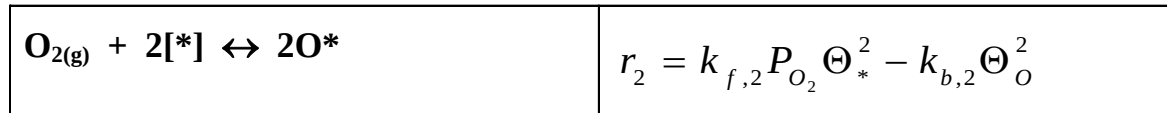
Elementary steps of catalytic CO oxidation on Pt

1. CO chemisorption

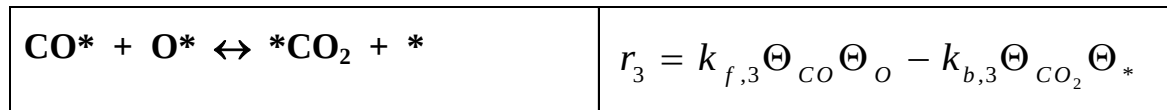


2. O₂ dissociative chemisorption

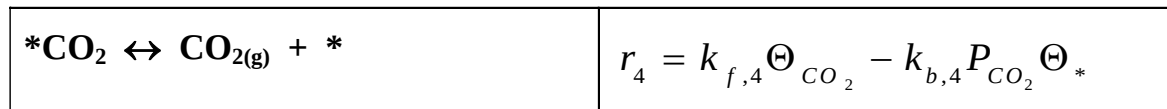
* - Pt surface atoms = Catalytic active centre



3. Surface reaction between CO* and O*



4. CO₂ desorption into gas phase



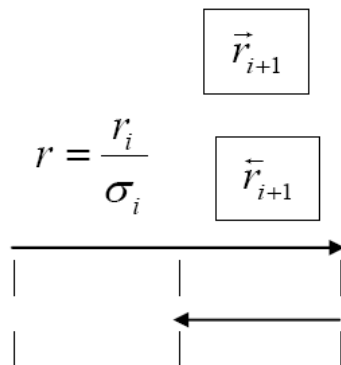
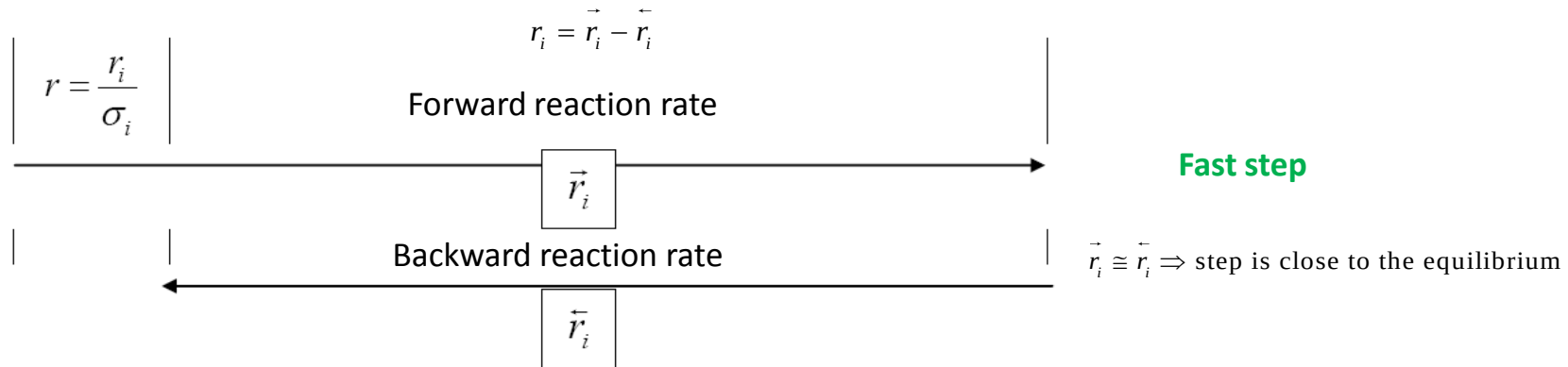
P_i – partial pressures of gaseous components [Pa]

Θ_i - occupancy (coverage) of the i-th species [-]

$k_{f,j}, k_{b,j}$ - reaction rate constants

r_j – rate of the j-th elementary step [mol/kg katalyzátoru/s
mol/molPt/s= 1/s]

Rate determining step in steady state



Slow step =
Rate determining step

Relation between overall reaction rate and the rate of i-th elementary step determines the stoichiometric number σ_i
(do not confuse with stoichiometric coefficient !)

$$r = \frac{r_i}{\sigma_i}$$

	σ_i
$\text{CO}_{(\text{g})} + [*] \leftrightarrow \text{CO}^*$	2
$\text{O}_{2(\text{g})} + 2[*] \leftrightarrow 2\text{O}^*$	1
$\text{CO}^* + \text{O}^* \leftrightarrow \text{*CO}_2 + *$	2
$\text{*CO}_2 \leftrightarrow \text{CO}_{2(\text{g})} + *$	2
$2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})}$	

M. Boudart, 1968, in “Kinetics of Chemical Processes”:

The stoichiometric number of i-th elementary step, σ_i is the number of times that this elementary step, as written, must be repeated, in the closed sequence, in order to obtain by summation of all steps the overall stoichiometric equation for reaction, as written.

Rate determining step: surface reaction

$$K_{CO} = \frac{k_{f,1}}{k_{b,1}} = \frac{\Theta_{CO}}{P_{CO} \Theta_*} \quad K_{O_2} = \frac{k_{f,2}}{k_{b,2}} = \frac{\Theta_O^2}{P_{O_2} \Theta_*^2} \quad K_{CO_2} = \frac{k_{b,4}}{k_{f,4}} = \frac{\Theta_{CO_2}}{P_{CO_2} \Theta_*}$$

$$\Theta_* + \Theta_{CO} + \Theta_O + \Theta_{CO_2} = 1$$

$$\Theta_* = \frac{1}{1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2}}$$

$$\Theta_{CO} = \frac{K_{CO} P_{CO}}{1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2}}$$

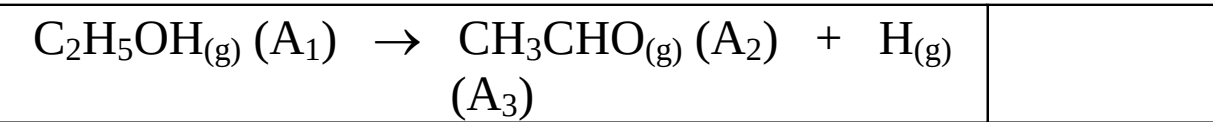
$$\Theta_O = \frac{\sqrt{K_{O_2} P_{O_2}}}{1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2}}$$

$$\Theta_{CO_2} = \frac{K_{CO_2} P_{CO_2}}{1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2}}$$

Reaction rate as a function of measurable variables

$$r_3 = k_{f,3} \Theta_{CO} \Theta_O - k_{b,3} \Theta_{CO_2} \Theta_* = \frac{k_{f,3} K_{CO} \sqrt{K_{O_2} P_{CO}} \sqrt{P_{O_2}} - k_{b,3} K_{CO_2} P_{CO_2}}{\left[1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2} \right]^2}$$

Example



catalysts: CuO, CoO a Cr₂O₃

(Franckaerts J., Froment G.F., Kinetic study of the dehydrogenation of ethanol, Chem. Eng. Sci. 19 (1964) 807-818).

Kinetics

$r_M = \frac{kK_1 (P_1 - P_2 P_3 / K_{eq})}{(1 + K_1 P_1 + K_2 P_2)^2}$	
---	--

r_M (mol.g⁻¹.hod⁻¹), P_i (bar), k (mol.g⁻¹.hod⁻¹), K_{eq} (bar), K_i (bar⁻¹).

Task: to estimate on the basis of experimental data kinetic and adsorption parameters k, K_1, K_2

EXPERIMENTAL SET-UP

Franckaerts J., Froment G.F., Kinetic study of the dehydrogenation of ethanol, Chem. Eng. Sci. 19 (1964) 807-818

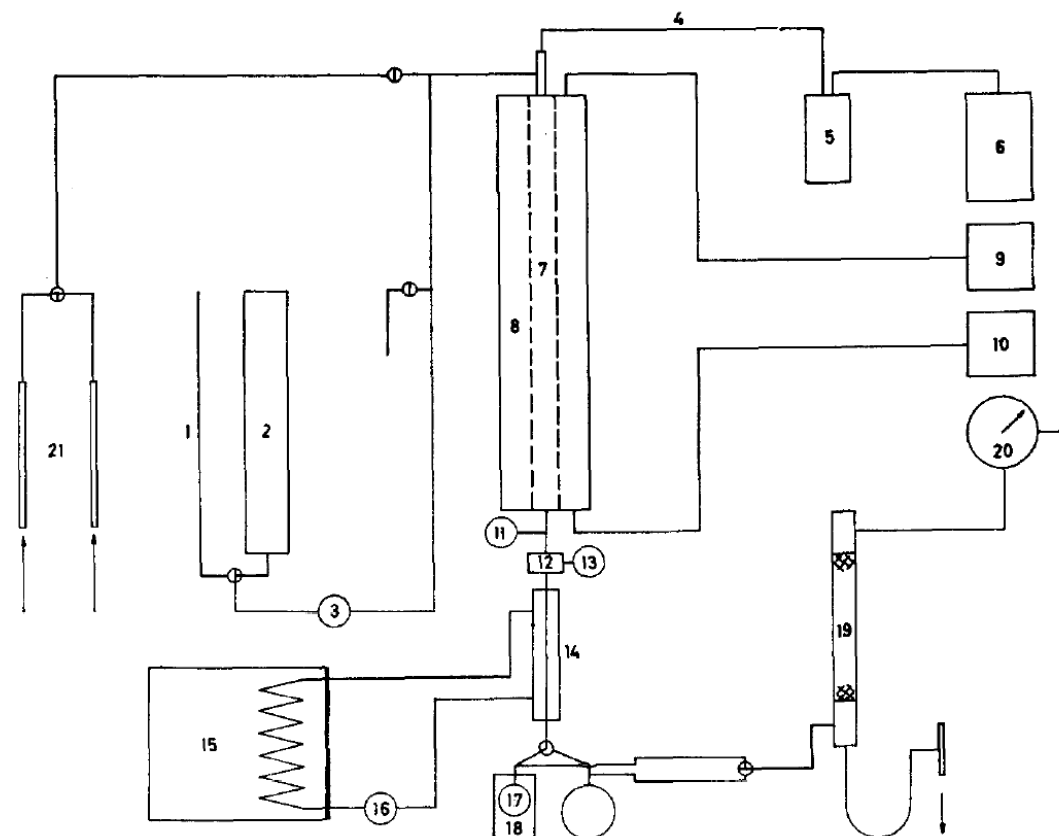


FIG. 1. Apparatus: 1,2, feed burettes; 3, metering pump; 4, thermocouples; 5, ice-bath; 6, mV-recorder; 7, reactor; 8, reactor-mantle; 9,10, variable transformers; 11,13, manometers; 12, pressure regulating device; 14, cooler; 15, cooling unit; 16, circulating pump; 17, sampling flask; 18, liquid air trap; 19, saturator, eventually also absorber in periods between sampling; 20, wet test meter; 21, flowmeters for air and nitrogen.

EXPERIMENTAL DATA

W / F_1^o [g.hod/mol]	P [bar]	y_1^o [–]	y_4^o [–]	y_2^o [–]	T [°C]	X_1 [–]
1,60	7,0	0,865	0,135	0,0	225,0	0,066
0,80	4,0	0,865	0,135	0,0	225,0	0,083
0,40	3,0	0,865	0,135	0,0	225,0	0,055
1,0	1,0	0,865	0,135	0,0	225,0	0,118
1,0	1,0	0,750	0,130	0,119	225,0	0,052
0,40	1,0	0,865	0,135	0,0	225,0	0,060
1,0	1,0	0,732	0,167	0,101	225,0	0,052
0,40	10,0	0,865	0,135	0,0	225,0	0,038
1,60	7,0	0,865	0,135	0,0	250,0	0,149
0,80	4,0	0,865	0,135	0,0	250,0	0,157
0,40	3,0	0,865	0,135	0,0	250,0	0,108
1,0	1,0	0,865	0,135	0,0	250,0	0,218
1,0	1,0	0,672	0,145	0,183	250,0	0,123
0,60	1,0	0,865	0,135	0,0	250,0	0,152
0,80	1,0	0,672	0,145	0,183	250,0	0,106
0,60	10,0	0,865	0,135	0,0	250,0	0,094
1,60	7,0	0,865	0,135	0,0	275,0	0,254
0,80	4,0	0,865	0,135	0,0	275,0	0,262
0,40	3,0	0,865	0,135	0,0	275,0	0,20
1,0	1,0	0,865	0,135	0,0	275,0	0,362
1,0	1,0	0,672	0,145	0,183	275,0	0,230
0,20	1,0	0,865	0,135	0,0	275,0	0,118
0,40	10,0	0,865	0,135	0,0	275,0	0,148
0,40	1,0	0,865	0,135	0,0	275,0	0,196

Solution:

Minimize the objective function:

$$\Phi(k, K_1, K_2) = \sum_{i=1}^{NEXP} \left[X_{1,i}^{\text{exp}} - X_{1,i}^{\text{mod}}(k, K_1, K_2) \right]^2$$

$X_{1,i}^{\text{mod}}(k, K_1, K_2)$ calculated from isothermal catalytic PFR model:

$$\frac{dX_1}{d(W / F_1^o)} = r_M(X_1) \quad W / F_1^o = 0, X_1 = 0$$

ATHENA Visual Studio.

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Příklad_9_1.aww - Athena Visual Studio
File Edit Model Build View Format Tools VisualKinetics Windows Help

! Catalytic Ethanol Dehydrogenation Kinetics
!-----
Global k1,KA1,KA2,KA3,KA4 As Real
Global TEMP, Press, Ymol(3) As Real

@Connect Variables
k1 =Par(1)           ! Reaction rate constant
KA1=Par(2)           ! Adsorption equilibrium constant for ethanol
KA2=Par(3)           ! Adsorption equilibrium constant for acetaldehyde
KA3=Par(4)           ! Adsorption equilibrium constant for hydrogen
KA4=Par(5)           ! Adsorption equilibrium constant for water
TEMP = Xu(6) + 273.15D0 ! Temperature [K]
Press = Xu(2)         ! Pressure [atm]
Ymol(1) = Xu(3)       ! Feed ethanol mol. fraction
Ymol(2) = Xu(4)       ! Feed water mol. fraction
Ymol(3) = Xu(5)       ! Feed acetaldehyde mol. fraction

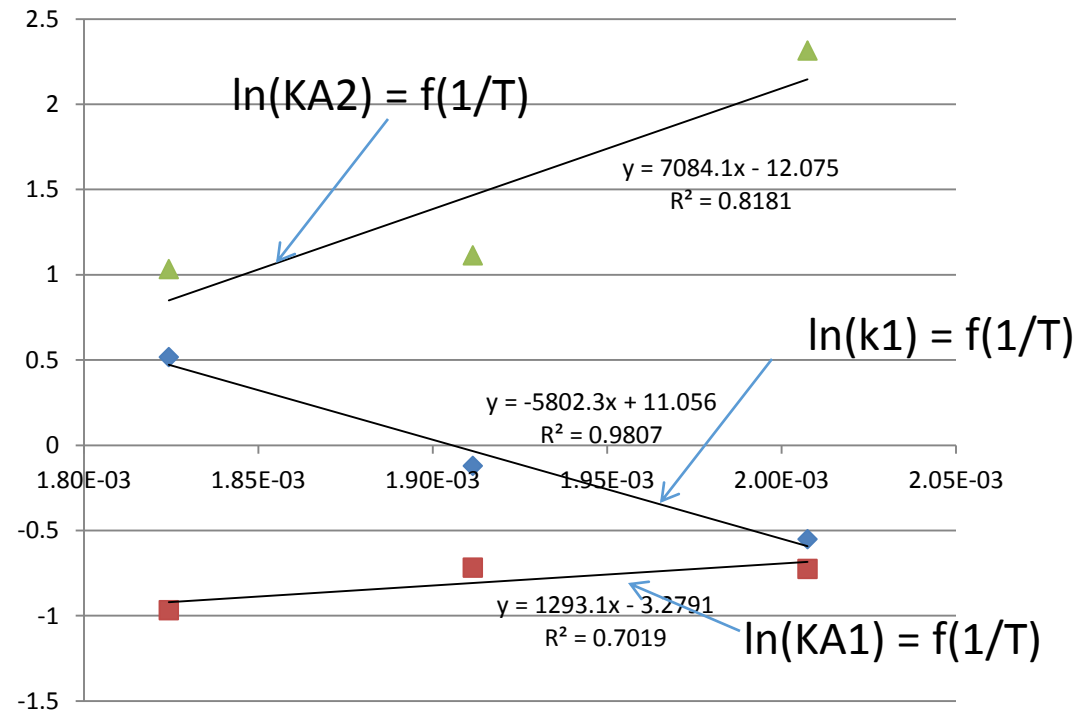
@Initial Conditions
U(1)=0.0

@Model Equations
Dim PA1, PA2, PA3, PA4, KEQ, X1, RR, AUX As Real
KEQ = DEXP (-14159.9D0/TEMP+25.2681D0)
X1 = U(1)
AUX = (1.0D0+Ymol(1)*X1)/Press
PA1 = Ymol(1)*(1.0D0-X1)/AUX ! Ethanol partial pressure
PA2 = (Ymol(3)+Ymol(1)*X1)/AUX ! Acetaldehyde partial pressure
PA3 = Ymol(1)*X1/AUX         ! Hydrogen partial pressure
PA4 = Ymol(2)/AUX           ! Water partial pressure
RR = k1*(PA1-PA2*PA3/KEQ)/(1.0D0+KA1*PA1+KA2*PA2+KA3*PA3+KA4*PA4)^2
F(1) = RR

@Response Model
Y(1)=U(1)

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```

	225 oC	250 oC	275 oC
k1	5.767986E-01 +- 4.112E-01	8.863130E-01 +- 1.668E-01	1.675828E+00 +- 4.225E-01
KA1	4.839934E-01 +- 3.591E-01	4.876108E-01 +- 9.443E-02	3.803293E-01 +- 1.473E-01
KA2	1.011693E+01 +- 7.376E+00	3.044445E+00 +- 9.054E-01	2.812096E+00 +- 1.078E+00



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10. Mass nad heat transfer in catalytic reactions

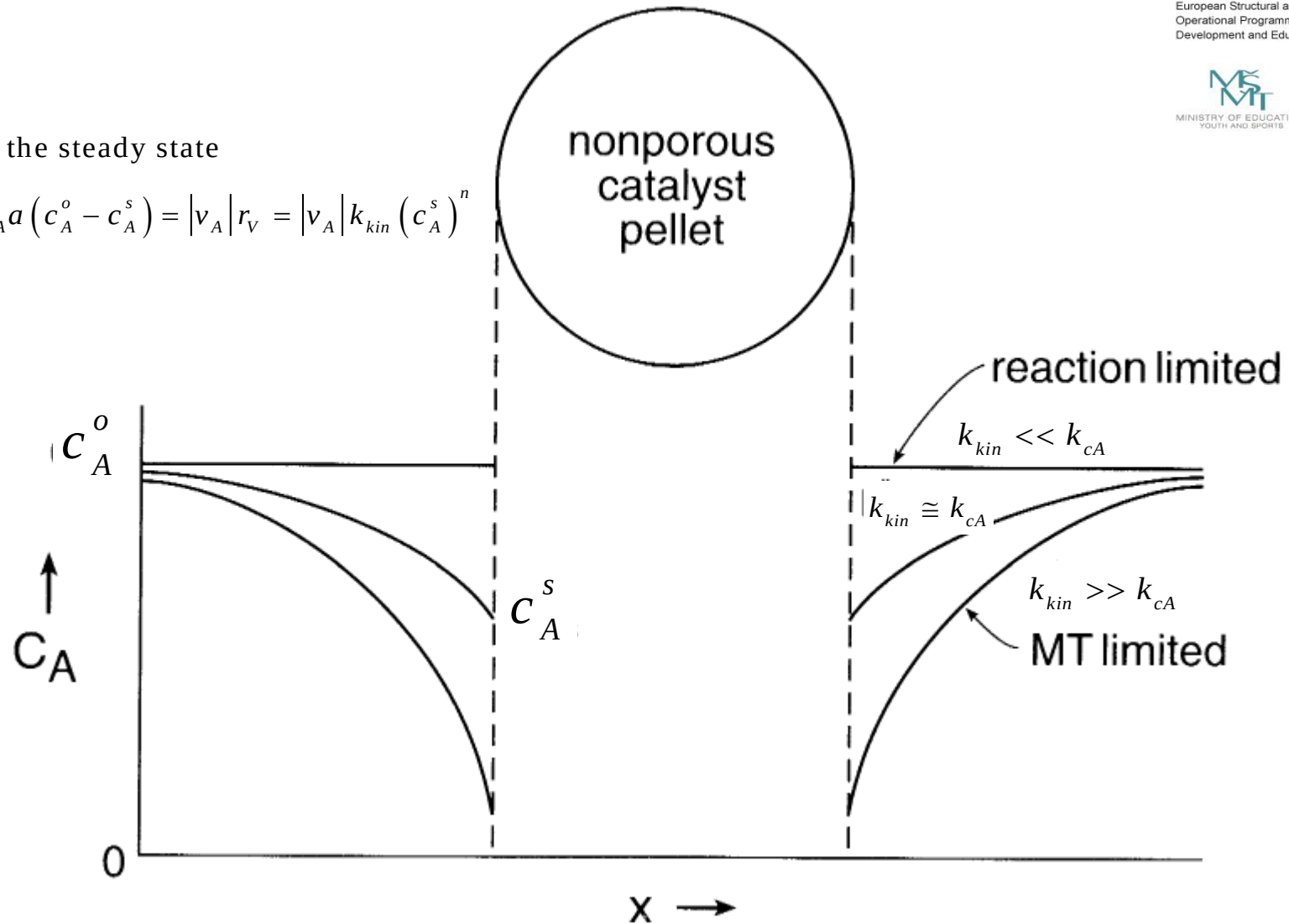


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In the steady state

$$k_{cA} a (c_A^o - c_A^s) = |v_A| r_V = |v_A| k_{kin} (c_A^s)^n$$



$$k_{cA}a(c_A^o - c_A^s) = k_{xA}a(x_A^o - x_A^s) = -\nu_A r_V = -(-1)r_V = r_V$$

$$r_V = k(T_s)(c_A^s)^n = k(T_o) \exp \left[-\frac{E}{RT_o} \left(\frac{T_o}{T_s} - 1 \right) \right] (c_A^s)^n =$$

$$= k(T_o) \exp \left[-\frac{E}{RT_o} \left(\frac{T_o}{T_s} - 1 \right) \right] (c_t)^n (x_A^s)^n$$

$$ha(T_s - T_o) = (-\Delta H_r)r_V$$

$$\frac{c_A^s}{c_A^o} = 1 - \frac{r_V}{k_{cA}ac_A^o}$$

$$\frac{x_A^s}{x_A^o} = 1 - \frac{r_V}{k_{xA}ax_A^o}$$

Effectiveness factor ($\bar{\eta}$)

$$\bar{\eta} = \frac{r_V(x_A^s, T_s)}{r_V(x_A^o, T_o)}$$

$$Da = \frac{r_V(x_A^o, T_o)}{k_{xA} a x_A^o} \quad \text{Damköhler number}$$

Surface/bulk molar fraction ratio

$$\frac{x_A^s}{x_A^o} = 1 - \frac{r_V}{k_{xA} a x_A^o} = 1 - \frac{\bar{\eta} r_V(x_A^o, T_o)}{k_{xA} a x_A^o} = 1 - \bar{\eta} Da$$

$\bar{\eta} Da = \frac{r_V}{k_{xA} a x_A^o}$ - measurable quantity $\Rightarrow \frac{x_A^s}{x_A^o}$ can be estimated from

experimental data

$$ha(T_s - T_o) = (-\Delta H_r)r_V = (-\Delta H_r)k_{xA}a(x_A^o - x_A^s)$$

$$\frac{T_s}{T_o} - 1 = (-\Delta H_r) \frac{k_{xA}x_A^o}{hT_o} \left(1 - \frac{x_A^s}{x_A^o}\right) \quad j_D = \frac{k_{cA}}{\bar{v}} Sc_A^{2/3} = a Re^{-b}$$

$$\frac{k_{xA}}{h} \text{ ratio:} \quad j_H = \frac{h}{c_{pM} \rho \bar{v}} Pr_A^{2/3} = a Re^{-b}$$

$$\frac{k_{xA}}{h} = \frac{j_D}{j_H} \frac{1}{\bar{C}_{pm} \bar{M}} \left(\frac{Pr}{Sc_A} \right)^{2/3} = \frac{j_D}{j_H} \frac{1}{\bar{C}_{pm} \bar{M}} \left(\frac{\bar{C}_{pm} \mu_m}{\lambda_m} / \frac{\mu_m}{\rho D_{im}} \right)^{2/3} =$$

$$= \frac{j_D}{j_H} \frac{1}{\bar{C}_{pm} \bar{M}} \left(\frac{\bar{C}_{pm} \rho D_{im}}{\lambda_m} \right)^{2/3} = \frac{j_D}{j_H} \frac{1}{\bar{C}_{pm} \bar{M}} Le_A^{-2/3}$$

$$Sh_A = \frac{k_{cA}d}{D_{Am}}, Nu = \frac{hd}{\lambda_m}$$

$$\frac{k_{cA}}{h} = \frac{k_{cA}}{h} = \frac{\frac{Sh_A D_{Am}}{d}}{\frac{Nu \lambda_m}{d}} = \frac{Sh_A}{Nu} \frac{D_{mA}}{\lambda_G} = \left(\frac{Sc_A}{Pr} \right)^{1/3} \frac{D_{mA}}{\lambda}$$

$$\begin{aligned}
 j_H / j_D &\cong 1 \quad \downarrow \\
 \frac{k_{xA}}{h} &= \frac{1}{\overline{C}_{pm} \overline{M}} Le_A^{-2/3} \quad Le_A = 1 - 1.1 \\
 \frac{T_s}{T_o} - 1 &= (-\Delta H_r) \frac{1}{\overline{C}_{pm} \overline{M}} Le_A^{-2/3} \frac{x_A^o}{T_o} \left(1 - \frac{x_A^s}{x_A^o}\right) = \\
 &= \overline{\beta} \overline{\eta} Da \\
 \overline{\beta} &= (-\Delta H_r) \frac{1}{\overline{C}_{pm} \overline{M}} Le_A^{-2/3} \frac{x_A^o}{T_o} \\
 \overline{\eta} Da &= \left(1 - \frac{x_A^s}{x_A^o}\right)
 \end{aligned}$$

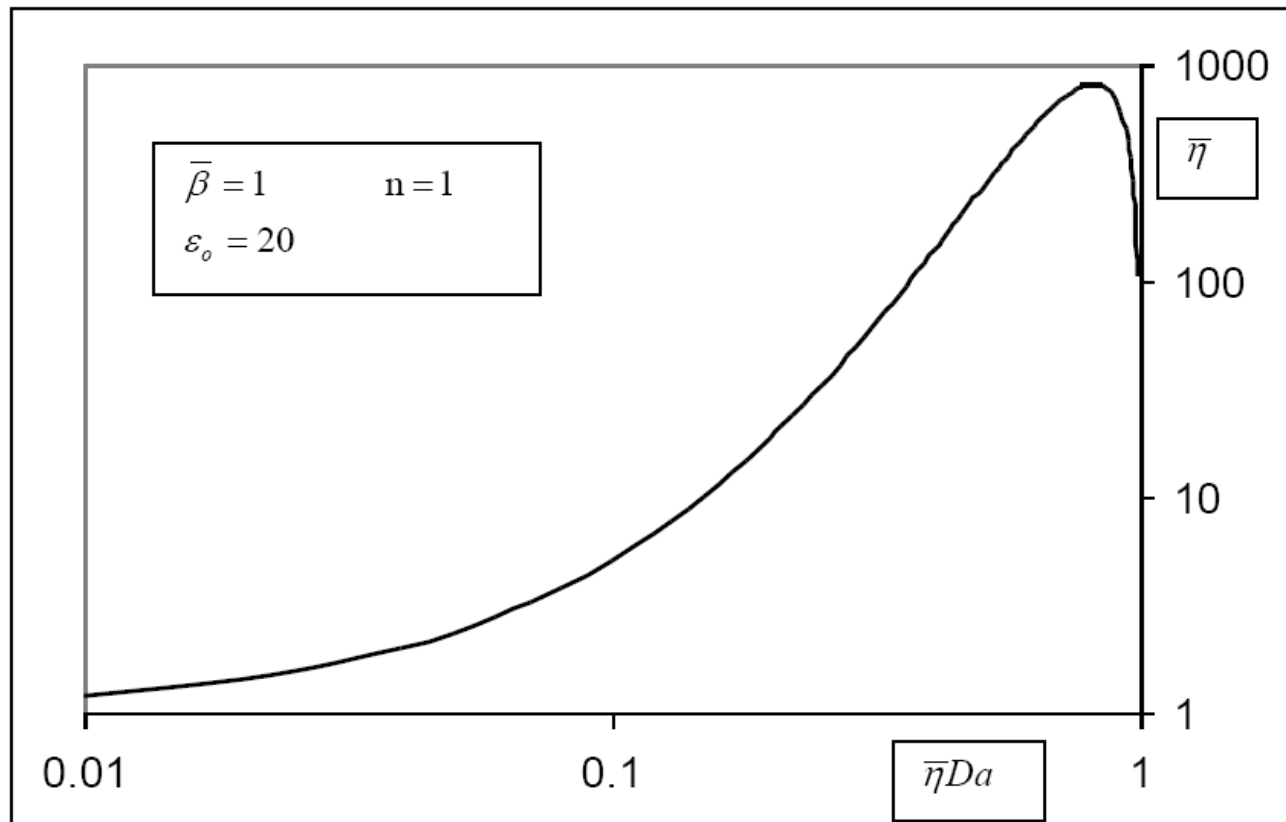
Maximal (minimal) temperature of surface

$$\left(\frac{T_s}{T_o} \right)_{\max, \min} - 1 = (-\Delta H_r) \frac{1}{\overline{C}_{pm} \overline{M}} Le_A^{-2/3} \frac{x_A^o}{T_o} = \overline{\beta}$$

$$r_V = k(T_s)(c_A^s)^n = \bar{\eta}k(T_o)(c_A^o)^n$$

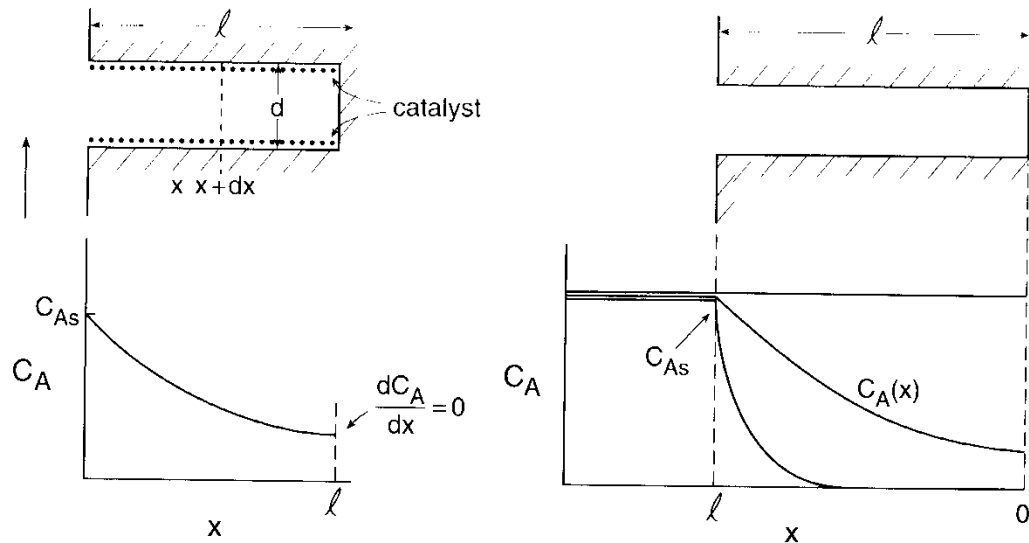
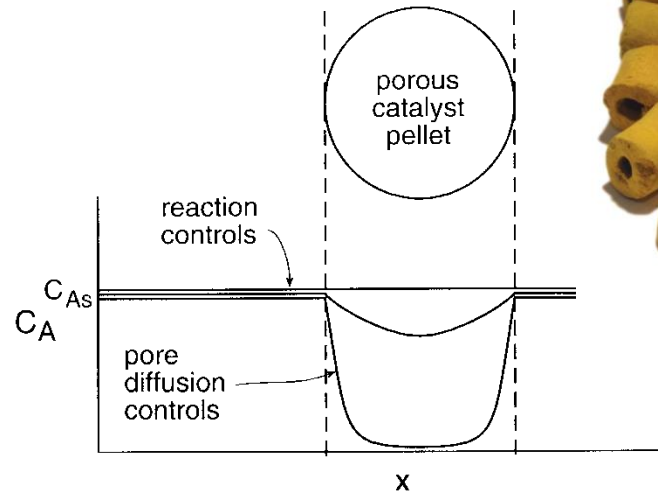
Effectiveness factor for external heat and mass transfer

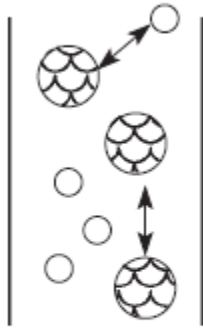
$$\begin{aligned}\bar{\eta} &= \frac{r_V(x_A^s, T_s)}{r_V(x_A^o, T_o)} = \exp\left[-\frac{E}{RT_o}\left(\frac{T_o}{T_s} - 1\right)\right] \left(\frac{c_t(T_s)}{c_t(T_o)}\right)^n \left(\frac{x_A^s}{x_A^o}\right)^n = \\ &= \exp\left[-\varepsilon_o\left(\frac{1}{1 + \beta\bar{\eta}Da} - 1\right)\right] \left(\frac{1}{1 + \beta\bar{\eta}Da}\right)^n (1 - \bar{\eta}Da)^n\end{aligned}$$



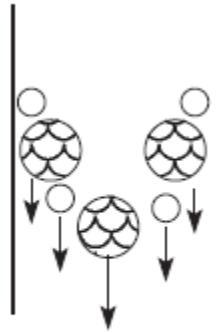
Internal mass transfer in porous catalytic particle

Figure 7-11 Reactant concentration profiles within a porous catalyst pellet for situations where surface reaction controls and where pore diffusion controls the reactions.





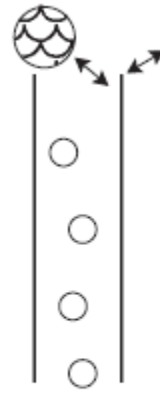
free
diffusion



viscous
flow



Knudsen
diffusion



molecular
sieving

Molecular diffusion

$$\vec{J}_i^D = -D_{i,m} \nabla c_i = -D_{i,m} \left(e_x \frac{\partial c_i}{\partial x} + e_y \frac{\partial c_i}{\partial y} + e_z \frac{\partial c_i}{\partial z} \right) \quad \text{Fick law}$$

Binary diffusion coefficient $D_{ij} = D_{ij}(T_o, P_o) \frac{P_o}{P} \left(\frac{T}{T_o} \right)^{n_D}$

Effective binary diffusion coefficient $D_{ij}^e = \frac{\varepsilon}{\tau} D_{ij}$

Knudsen diffusion

$$\vec{J}_i^K = -D_i^K \nabla c_i = -D_i^K \left(e_x \frac{\partial c_i}{\partial x} + e_y \frac{\partial c_i}{\partial y} + e_z \frac{\partial c_i}{\partial z} \right)$$

Knudsen diffusion coefficient $D_i^K = D_i^K(T_o) \sqrt{\frac{T}{T_o}}$

Effective Knudsen diffusion coefficient $D_i^{K,e} = \frac{\varepsilon}{\tau} D_i^K$

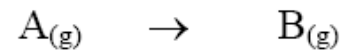
Viscous (convective) flow

$$\vec{J}_i^V = -\frac{y_i B_o P}{\mu R T} \nabla P$$

Total flow

$$\vec{J}_i = \vec{J}_i^D + \vec{J}_i^K + \vec{J}_i^V$$

First order gas phase reaction



Reaction rate

$$r_S = k_S c_A [\text{mol.m}^{-2}.\text{s}^{-1}]$$

Balance of component A in cylindrical pore

$$\overline{D}_A \frac{d^2 c_A}{dx^2} = \frac{4}{d_p} k_S c_A$$

$$\frac{1}{\overline{D}_A} = \frac{1}{D_A^K} + \frac{1}{D_{AB}}$$

Boundary conditions

$$x = L$$

$$c_A = c_A^s$$

$$x = 0$$

$$\frac{dc_A}{dx} = 0$$

Solution

$$c_A(x) = B_1 e^{\alpha x} + B_2 e^{-\alpha x}$$

$$\alpha = \sqrt{\frac{4k_s}{d_p \bar{D}_A}}$$

$$c_A^s = B_1 e^{\alpha L} + B_2 e^{-\alpha L}$$

$$0 = B_1 - B_2$$

$$B_1 = B_2 = \frac{c_A^s}{e^{\alpha L} + e^{-\alpha L}}$$

$$c_A(x) = \frac{c_A^s}{e^{\alpha L} + e^{-\alpha L}} [e^{\alpha x} + e^{-\alpha x}] = c_A^s \frac{e^{\alpha x} + e^{-\alpha x}}{e^{\alpha L} + e^{-\alpha L}} = c_A^s \frac{\cosh(\alpha x)}{\cosh(\alpha L)}$$

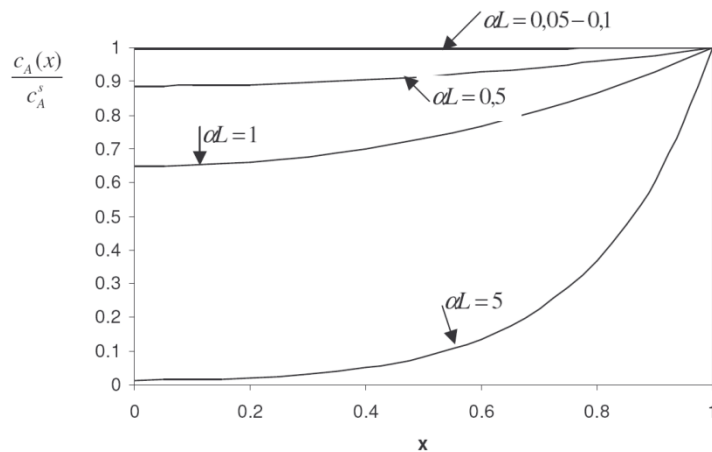
Mean reaction rate in the pore (rate of consumption of A)

$$R_A = \pi d_p \int_0^L k_s c_A dx = \frac{\pi d_p k_s c_A^s}{e^{\alpha L} + e^{-\alpha L}} \left[\frac{1}{\alpha} e^{\alpha x} - \frac{1}{\alpha} e^{-\alpha x} \right]_0^L = \frac{\pi d_p k_s c_A^s}{\alpha} \frac{e^{\alpha L} - e^{-\alpha L}}{e^{\alpha L} + e^{-\alpha L}} = \frac{\pi d_p k_s c_A^s}{\alpha} \tanh(\alpha L)$$

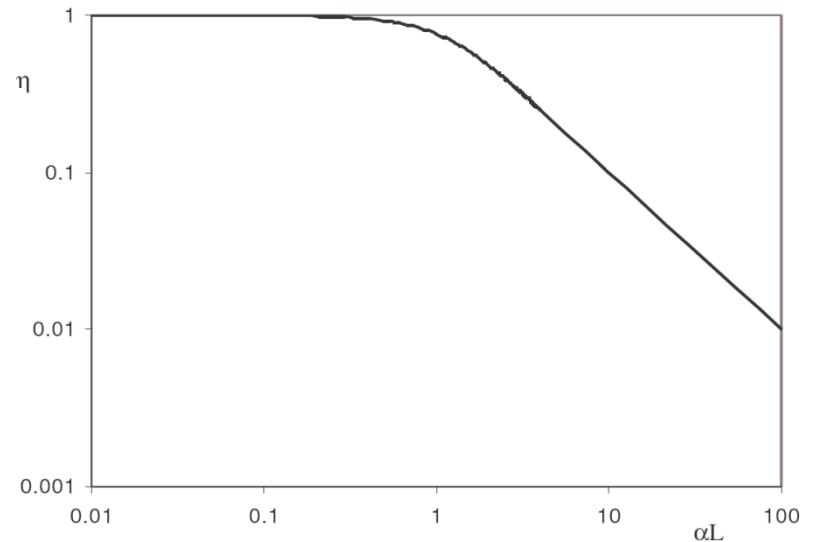
[mol A/s]

Effectiveness factor

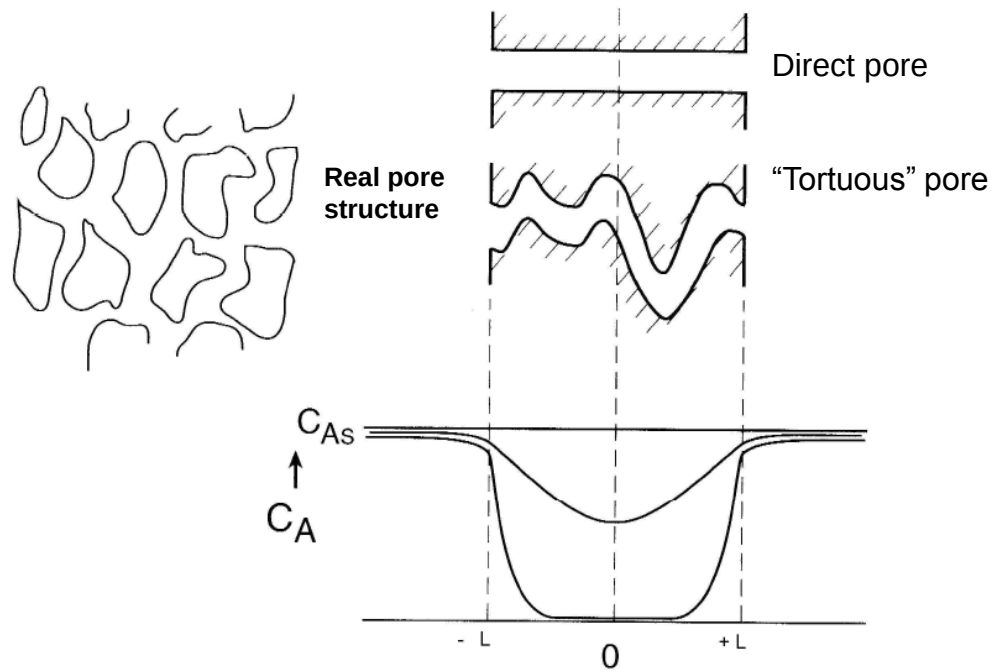
$$\eta = \frac{R_A}{R_A(c_A^s)} = \frac{\frac{\pi d_p k_s c_A^s}{\alpha} \tanh(\alpha L)}{\pi d_p L k_s c_A^s} = \frac{\tanh(\alpha L)}{\alpha L}$$



Závislost koncentrace složky A na souřadnici x.



Závislost účinnostního faktoru na αL



Real catalytic particle in the form of slab

$$\bar{D}_{eA} \frac{d^2 c_A}{dx^2} = S_g \rho k_s c_A$$

$$\frac{1}{\bar{D}_{eA}} = \frac{1}{D_{eA}^K} + \frac{1}{D_{eAB}}$$

$$x = l$$

$$c_A = c_A^s$$

$$x = 0$$

$$\frac{dc_A}{dx} = 0$$

Dimensionless variables

$$Y = \frac{c_A}{c_A^s} \quad z = \frac{x}{l}$$

$$\frac{d^2 Y}{dz^2} = \Phi^2 Y$$

$$z = 0 \quad \frac{dY}{dz} = 0 \quad z = 1 \quad Y = 1$$

$$\Phi = l \sqrt{\frac{S_g \rho k_s}{\bar{D}_A}}$$

Thiele number
(module)

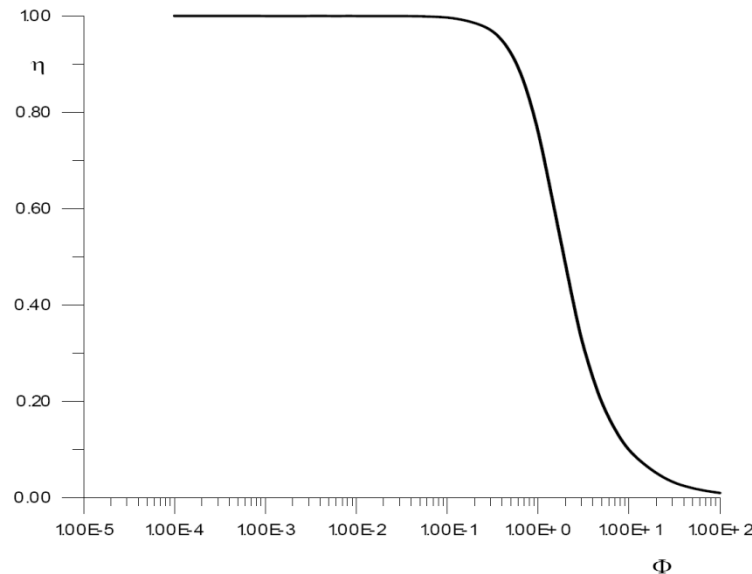
Solution

$$Y(z) = \frac{\cosh(\Phi z)}{\cosh(\Phi)}$$

$$\begin{aligned}
 \eta &= \frac{2\rho S S_g k \int_0^L c_A dx}{2\rho S L S_g k c_A^o} = \\
 &= \int_0^1 \frac{c_A}{c_A^o} d\left(\frac{x}{L}\right) = \int_0^1 Y dz = \frac{1}{\cosh(\Phi)} \int_0^1 [\cosh(\Phi z)] dz = \frac{1}{\Phi} \frac{\sinh(\Phi)}{\cosh(\Phi)} = \\
 &= \frac{\tanh(\Phi)}{\Phi}
 \end{aligned}$$

Real reaction rate

$$\bar{R}_A = \eta 2\rho S L S_g k c_A^o = \frac{\tanh(\Phi)}{\Phi} 2\rho S L S_g k c_A^o$$

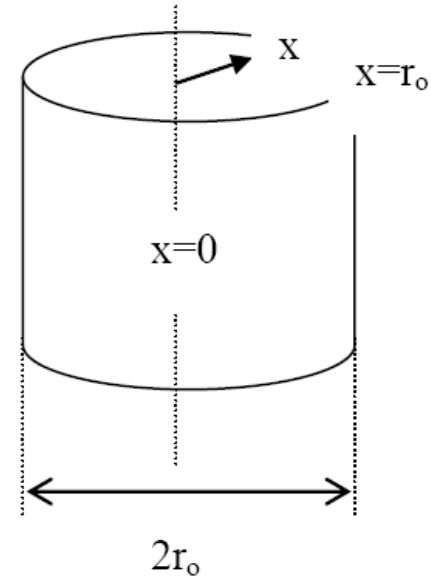


Effectiveness factor as a function of Thiele number

Cylinder

$$\bar{D}_{eA} \left[\frac{d^2 c_A}{dx^2} + \frac{1}{x} \frac{dc_A}{dx} \right] = S_g \rho k_s c_A$$

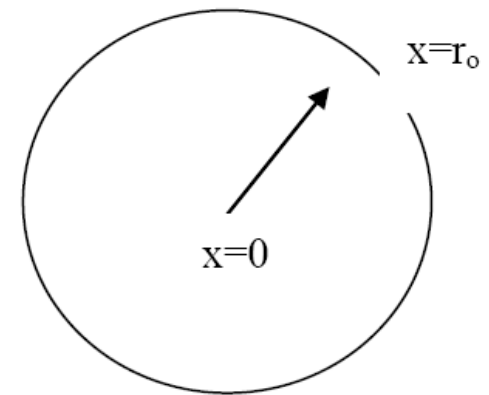
$$x=0 \quad \frac{dc_A}{dx} = 0 \quad x=r_o \quad c_A = c_A^s$$



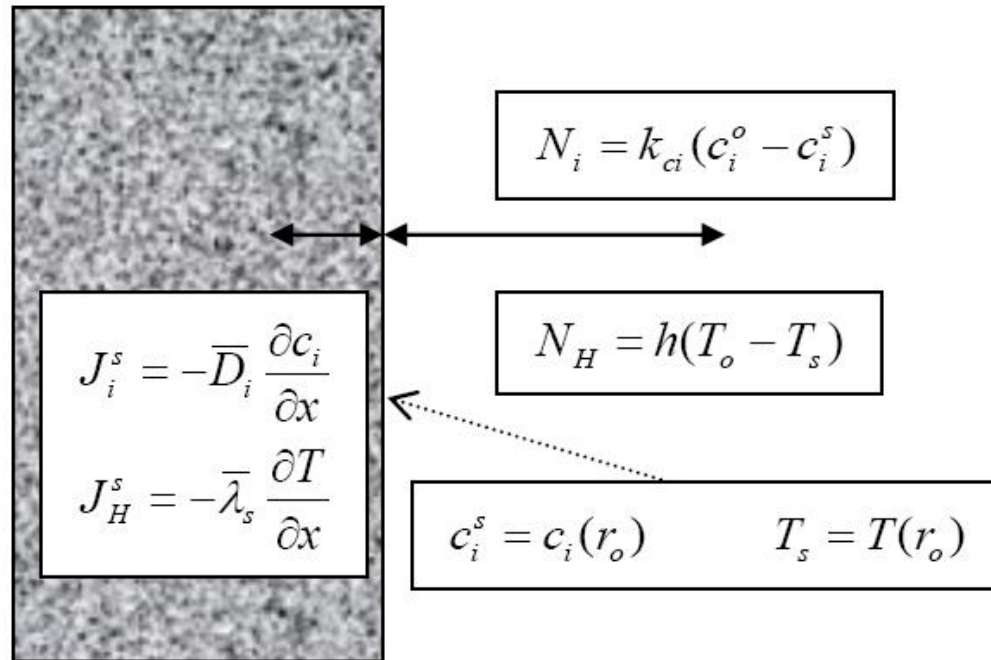
Sphere

$$\bar{D}_{eA} \left[\frac{d^2 c_A}{dx^2} + \frac{2}{x} \frac{dc_A}{dx} \right] = S_g \rho k_s c_A$$

$$x=0 \quad \frac{dc_A}{dx} = 0 \quad x=r_o \quad c_A = c_A^s$$



Heat and mass transfer



Balance equations

$$\bar{D}_i \left(\frac{d^2 c_i}{dx^2} + \frac{a}{x} \frac{dc_i}{dx} \right) = -v_i r_V(T, c_k)$$

$$a = \begin{array}{ll} 0 & \text{Slab} \\ 1 & \text{Cylinder} \\ 2 & \text{Sphere} \end{array}$$

$$\bar{\lambda}_s \left(\frac{d^2 T}{dx^2} + \frac{a}{x} \frac{dT}{dx} \right) = (\Delta H_r) r_V(T, c_k)$$

Boundary conditions

$x = 0$

$$\frac{dc_i}{dx} = 0$$

$$\frac{dT}{dx} = 0$$

$x = r_o$

$$-\bar{D}_i \frac{dc_i}{dx} = k_{ci} (c_i^s - c_i^o)$$

$$-\bar{\lambda}_s \frac{dT}{dx} = h(T_s - T_o)$$

Maximal temperature gradient in particle of catalyst(Prater 1958)

Elimination of r_v from enthalpy balance:

$$\bar{\lambda}_s \frac{1}{x^a} \frac{d}{dx} \left(x^a \frac{dT}{dx} \right) = (\Delta H_r) \bar{D}_i \frac{1}{x^a} \frac{d}{dx} \left(x^a \frac{dc_i}{dx} \right)$$

$$\int_{x=0}^x \frac{d}{dx} \left(x^a \frac{dT}{dx} \right) dx = \frac{(\Delta H_r) \bar{D}_i}{\bar{\lambda}_s} \int_{x=0}^x \frac{d}{dx} \left(x^a \frac{dc_i}{dx} \right) dx$$

$$x^a \left(\frac{dT}{dx} \right) = \frac{(\Delta H_r) \bar{D}_i}{\bar{\lambda}_s} x^a \left(\frac{dc_i}{dx} \right)$$

$$T(x) - T(0) = \frac{(\Delta H_r) \bar{D}_i}{\bar{\lambda}_s} (c_i(x) - c_i(0))$$

$$c_i(0) \rightarrow 0 \quad \text{or} \quad c_i(0) \rightarrow c_i^{eq} \Rightarrow T(x) - T(0) \rightarrow \Delta T_{\max}$$

$$\Delta T_{\max} = T(r_o) - T(0) = \frac{(\Delta H_r) \bar{D}_i}{\bar{\lambda}_s} c_i(r_o) = \frac{(\Delta H_r) \bar{D}_i}{\bar{\lambda}_s} c_i^s$$

$$-\frac{\Delta T_{\max}}{T_o} = \frac{T(0) - T(r_o)}{T_o} = \frac{(-\Delta H_r) \bar{D}_i}{\bar{\lambda}_s T_o} c_i^s = \bar{\beta}$$

Prater C.D., The temperature produced by heat of reaction in the interior of porous particles, Chem. Eng. Sci. 8 (1958) 284.

The temperature produced by heat of reaction in the interior of porous particles

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(Received 9 September 1957)

Abstract—Heat of reaction will cause a temperature difference to occur between the inside and boundary of a porous particle during an internal reaction. An equation is derived relating this temperature difference to the reactant concentration difference, and it is shown to be independent of the kinetics of the reaction and of the particle geometry. Examples are given of the application of this equation to cyclohexane dehydrogenation and catalyst regeneration.

Résumé—La chaleur de réaction produira une différence de température entre la surface limite et l'intérieur de particules poreuses, au cours de réactions au sein de cette particule. Une équation est obtenue établissant la relation entre cette différence de température et la différence de concentration des composés réagissant. Elle est indépendante de la cinétique de la réaction et de la forme géométrique des particules. Les exemples d'application de cette équation sont donnés pour la désydrogénation du cyclohexane et la régénération de catalyseurs.

Zusammenfassung—Die Reaktionswärme erzeugt eine Temperaturdifferenz zwischen dem Inneren und der Aussenseite eines porösen Teilchens während einer inneren Reaktion. Es wird eine Gleichung abgeleitet, um diese Temperaturdifferenz auf die Konzentrationsdifferenz des Reaktanten zu beziehen und es wird gezeigt, dass sie unabhängig von der Reaktionskinetik und der Teilchengometrie ist. Für die Anwendung dieser Gleichung werden als Beispiele die Dehydrierung von Cyclohexan und die Regeneration eines Katalysators behandelt.

INTRODUCTION

MANY of the reactions which occur within porous catalytic solids have an appreciable heat of reaction. This heat of reaction will give rise to a temperature difference between the inside and boundary of the catalyst particle while the reaction is proceeding. An estimate of the size of this difference is needed in many catalytic investigations. A complete solution of the problem would give the temperature as a function of the spatial co-ordinates of the particle. To obtain this, a separate solution is required for each particle shape, boundary condition and kinetics. It is not possible to obtain such solutions in a closed form except for certain special cases and, in general, numerical methods must be used.

It will be shown that a solution can be obtained which is valid for all kinetics and all particle geometries. This solution gives the temperature as a function of the concentration of reactant. Information has been sacrificed to obtain this generality, namely, the temperature as a function of co-ordinates. This solution is:—

$$(T - T_s) = \frac{-\Delta H D_e}{K} (c_s - c) \quad (1)$$

where T is the centigrade temperature at all points within the particle which have a concentration of reactant c (mole/cm³)

T_s is the temperature (°C) at the surface of the particle

c_s is the concentration of the reactant at the surface of the particle (mole/cm³)

ΔH is the heat of reaction (cal/mole) (negative values mean exothermic reactions)

D_e is the effective diffusivity of the particle (cm²/sec)

K is the thermal conductivity of the particle (cal/sec cm °C)

DAMKOHLER [1] and WHEELER [2] have investigated the thermal effects in spherical particles and have obtained the same equation for this special case. The derivation given below will show that the equation holds for particles of any shape.

The maximum possible temperature difference

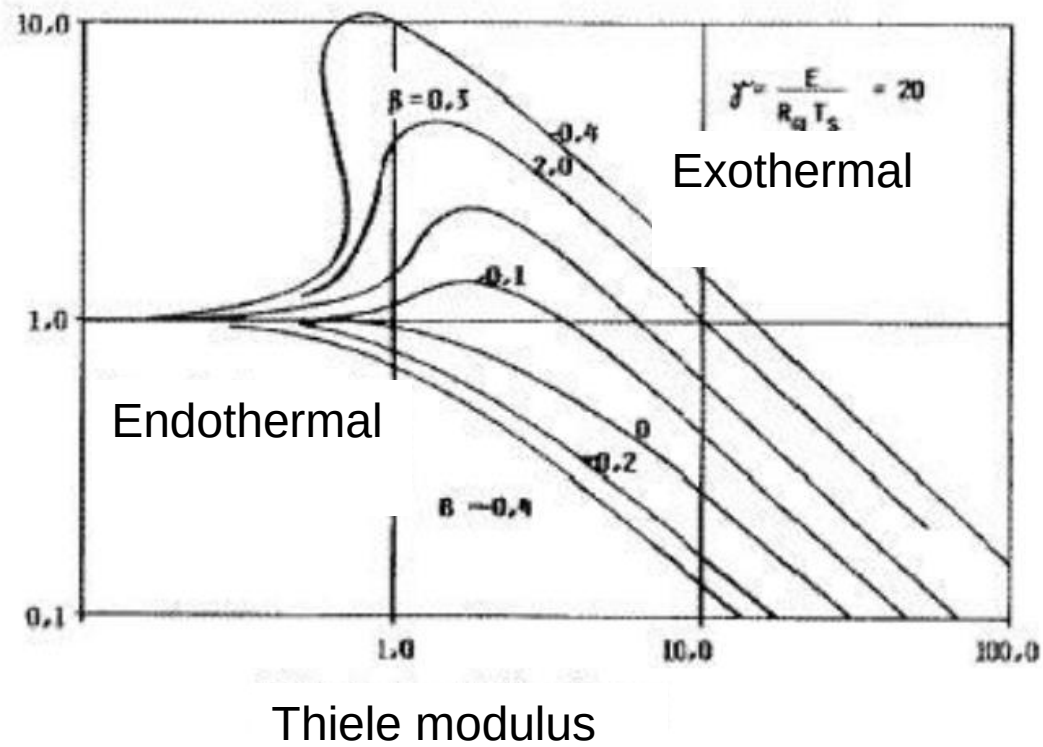
The next reaction to be considered is the dehydrogenation of *cyclohexane* over a commercial platinum-alumina reforming catalyst. This is an endothermic reaction with a ΔH of $+ 52.54 \times 10^3$ cal/mole at 400°C . The conditions are 400°C reaction temperature, 4:1 hydrogen to hydrocarbon ratio and 25 atmospheres total pressure. The values of the constants for this catalyst are —

$$D_e = 15.6 \times 10^{-3} \text{ cm/sec}^2 \text{ (cyclohexane at } 400^\circ\text{C)}$$

$$K = 5.3 \times 10^{-4} \text{ cal/sec cm } ^\circ\text{C}.$$

The value of the equilibrium concentration of *cyclohexane* is calculated from free energy data given by ROSSINI *et al.* [5]. The calculated maximum temperature drop possible is found to be 53°C which will be quite important in kinetic studies. Thus further study to determine the actual temperature distribution in the particles may be desirable.

In the above discussion, the problem of the measurement of the particle boundary temperature has not been considered explicitly. Conventionally, the temperature measuring device is located externally to the particle. The question then arises as to how well the temperature measured by the device represents the actual temperature of the particle boundary. A consideration of the particular conditions existing in a given experiment is needed to answer this question.



Effectiveness factor for non isothermal catalytic particle

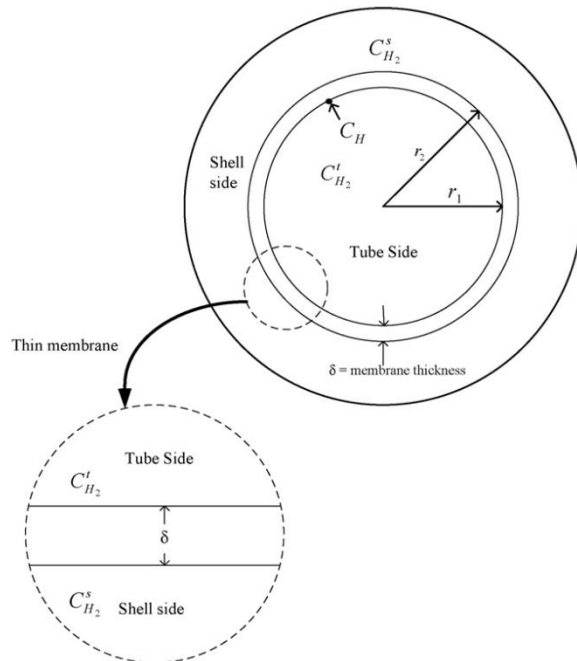
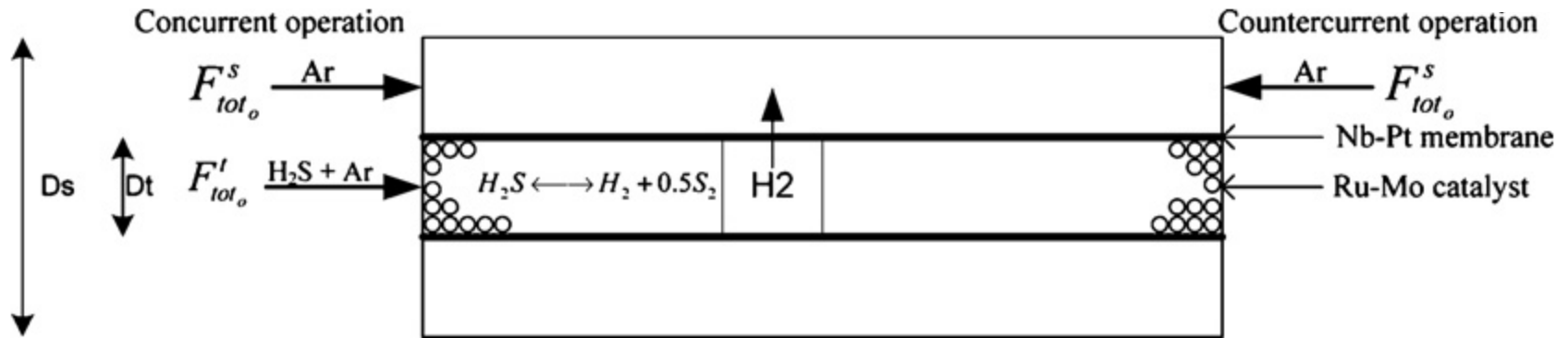
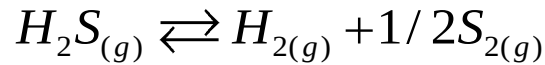
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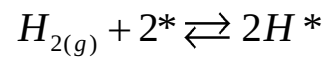
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11. Catalytic membrane reactor



Dissociative chemisorption and diffusion in (Nb-Pt) membrane



$$K_H = \frac{C_H^2}{P_{H_2} C_*^2}$$

$$C_H + C_* = C_H^o$$

C_H^o – solubility of H_2 in membrane

$$\Rightarrow C_H = \frac{C_H^o \sqrt{K_H P_{H_2}}}{1 + \sqrt{K_H P_{H_2}}} \cong C_H^o \sqrt{K_H P_{H_2}}$$

Hydrogen flux through Nb-Pt membrane

$$J_{H_2}^{memb} = -D_{H_2}^{memb} \frac{dC_H}{dr}$$

$$F_{H_2}^{memb} = 2\pi r \Delta x J_{H_2}^{memb} = 2\pi r \Delta x \left[-D_{H_2}^{memb} \frac{dC_H}{dr} \right]$$

$$F_{H_2}^{memb} \int_{r_1}^{r_2} \frac{dr}{r} = 2\pi \Delta x \left[-D_{H_2}^{memb} \int_{\Theta_1}^{\Theta_2} dC_H \right]$$

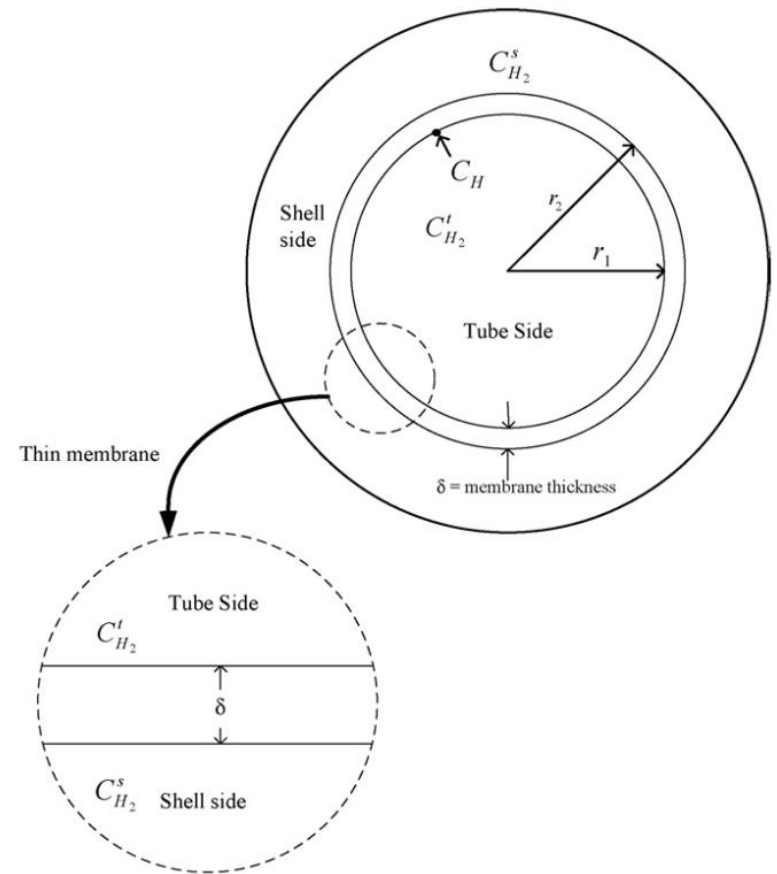
$$F_{H_2}^{memb} \ln \frac{r_2}{r_1} = 2\pi \Delta x D_{H_2}^{memb} (C_H(r_1) - C_H(r_2))$$

$$F_{H_2}^{memb} = \frac{2\pi D_{H_2}^{memb}}{\ln \frac{r_2}{r_1}} \Delta x (C_H(r_1) - C_H(r_2)) =$$

$$= \frac{2\pi D_{H_2}^{memb} C_H^o \sqrt{K_H}}{\ln \frac{r_2}{r_1}} \Delta x (\sqrt{P_{H_2}(r_1)} - \sqrt{P_{H_2}(r_2)})$$

$$\frac{F_{H_2}^{memb}}{2\pi r_1 \Delta x} = J_{H_2}^{memb}(r_1) = \frac{D_{H_2}^{memb} C_H^o \sqrt{K_H}}{r_1 \ln \frac{r_2}{r_1}} (\sqrt{P_{H_2}(r_1)} - \sqrt{P_{H_2}(r_2)}) = \frac{\Gamma_{H_2}^{(1)}}{\delta} (\sqrt{P_{H_2}(r_1)} - \sqrt{P_{H_2}(r_2)})$$

$\Gamma_{H_2}^{(1)} / \delta$



$$\Gamma_{H_2}^{(1)} = \frac{0.043122}{T} - 3.0484 \times 10^{-5} \quad (\text{mole} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{kPa}^{-0.5})$$

Balance of hydrogen in tube side (catalyst)

H₂

$$\frac{dF_{H_2}}{dx} = v_{H_2} r_M \rho_b \pi r_1^2 - 2\pi r_1 J_{H_2}^{memb}(r_1) = v_{H_2} r_M \rho_b \pi r_1^2 - 2\pi r_1 \frac{\Gamma_{H_2}^{(1)}}{\delta} \left(\sqrt{P_{H_2}(r_1)} - \sqrt{P_{H_2}(r_2)} \right)$$

other components

$$\frac{dF_i}{dx} = v_i r_M \rho_b \pi r_1^2$$

$$r_M = k(T) \left(P_{H_2S} - P_{H_2} P_{S_2}^{1/2} / K^{eq}(T) \right) \quad (\text{mol.g}^{-1}.\text{s}^{-1})$$

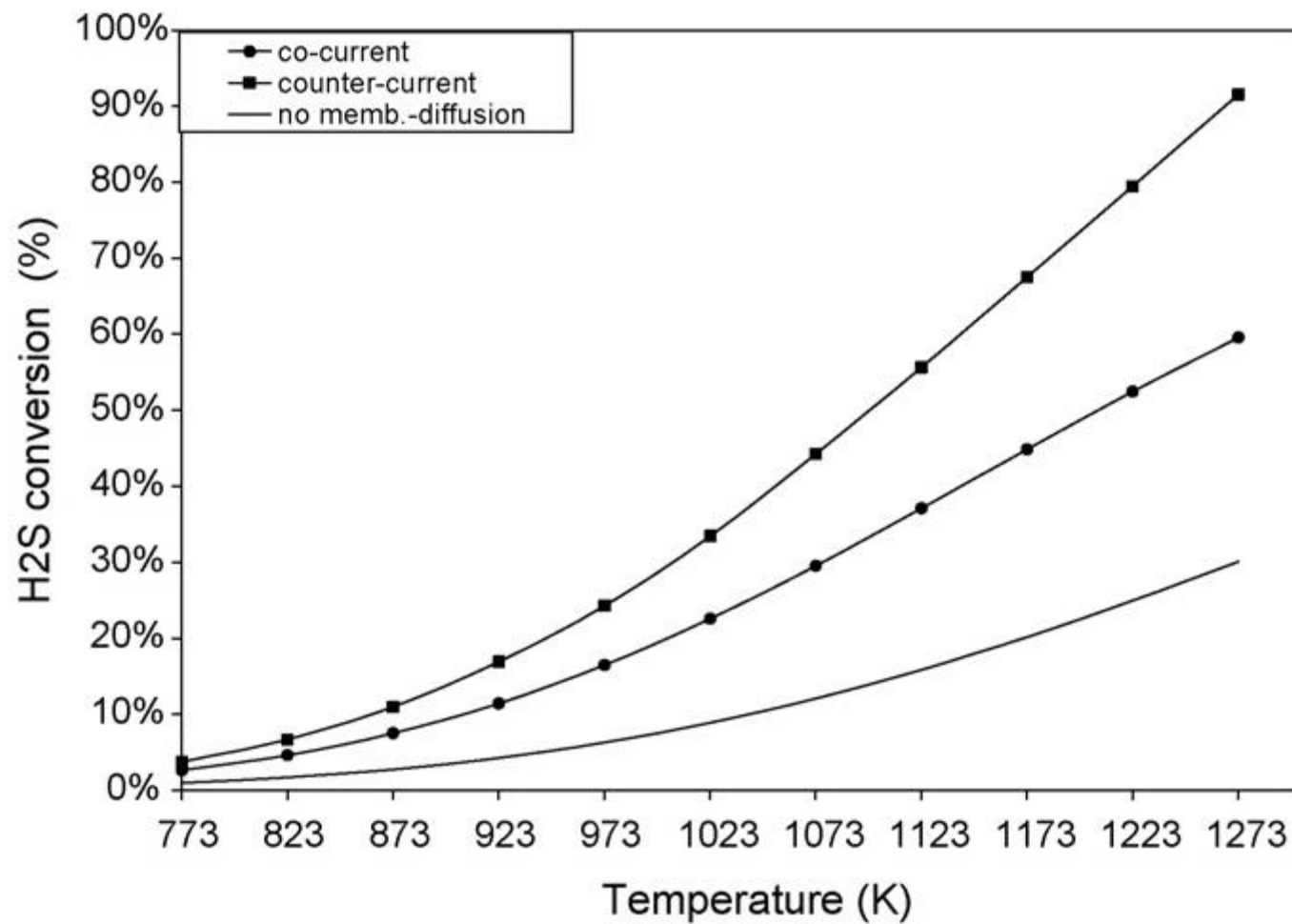
$$k(T) = 0.038505 \exp \left(-\frac{87220}{RT} \right) \quad (\text{mol.g}^{-1}.\text{s}^{-1}.\text{kPa}^{-1})$$

$$K^{eq}(T) = 3782 \exp \left(-\frac{10871}{T} \right) \quad (\text{kPa}^{1/2})$$

Balance of hydrogen in shell-side

co-current (+), contre-current (-)

$$\frac{dF_{H_2}}{dx} = \pm 2\pi r_2 J_{H_2}^{memb}(r_2) = \pm 2\pi r_2 \frac{\Gamma_{H_2}^{(2)}}{\delta} \left(\sqrt{P_{H_2}(r_1)} - \sqrt{P_{H_2}(r_2)} \right)$$



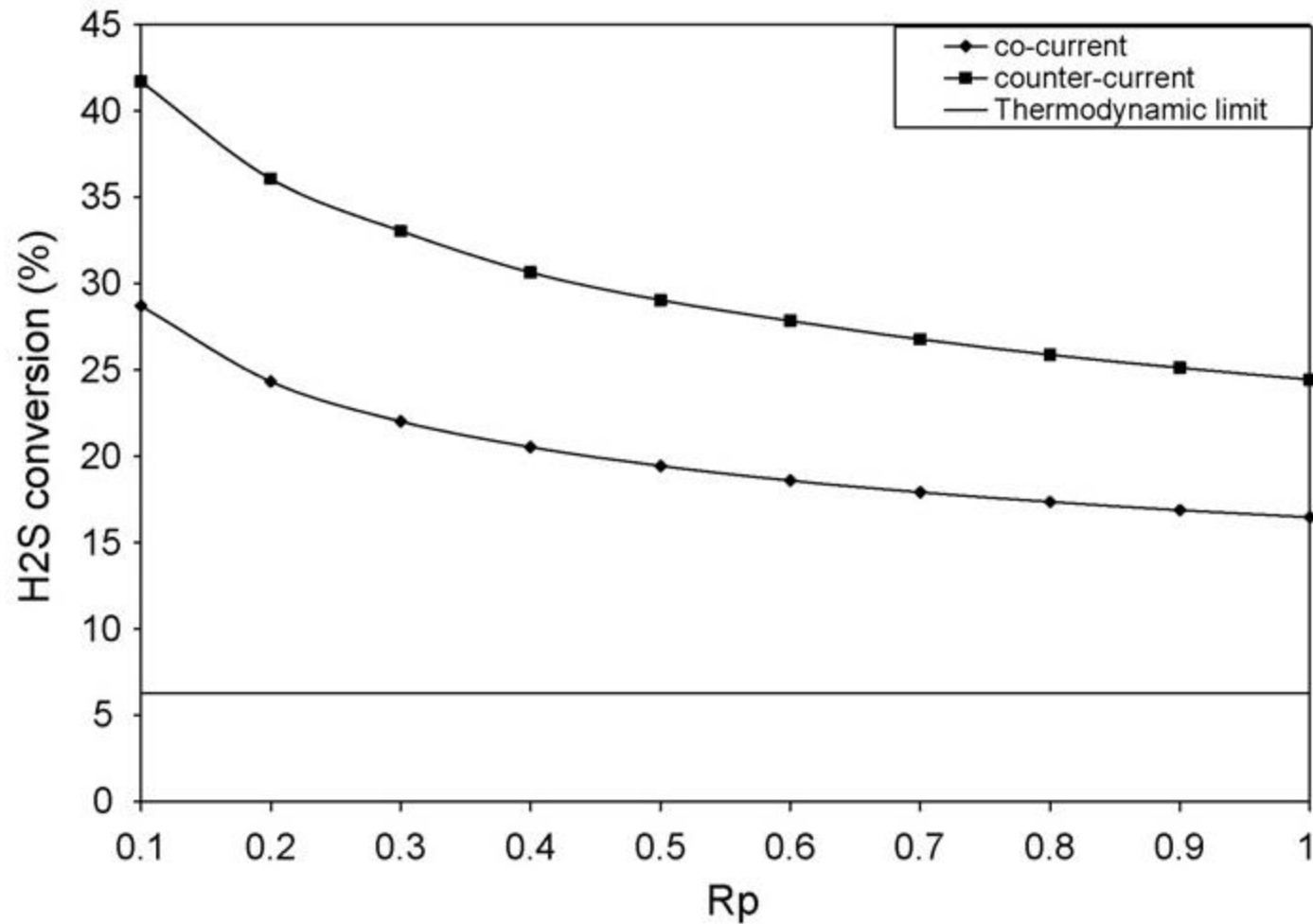


Fig. 6. Effect of shell-tube side pressure ratio on H₂S conversion at $T_0^t = 973$ K, $r_{tt} = 600$ s, $r_{ts} = 600$ s ($Da_0^t = 319$, $Tu_0 = 3.8$).



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Catalytic decomposition of H₂S in a double-pipe packed bed membrane reactor: Numerical simulation studies

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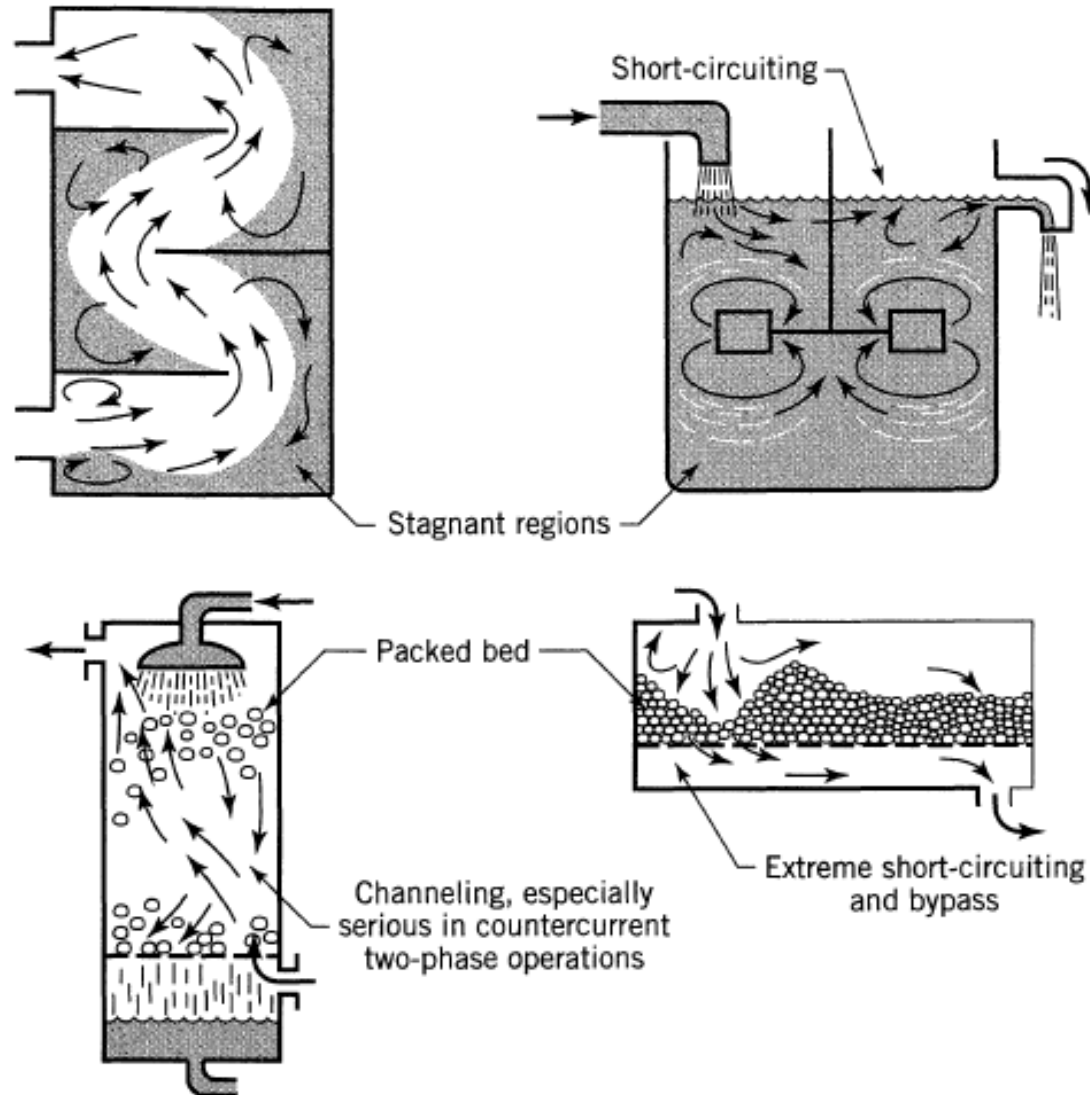
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12. Non ideal flow, residence time distribution

- The three main reactor types developed thus far - batch, continuous-stirred-tank, and plug-flow reactors - are useful for modeling many complex chemical reactors.
- Up to this point we have neglected a careful treatment of the fluid flow pattern within the reactor.
- In this lecture we explore some of the limits of this approach and develop methods to address and overcome some of the more obvious limitations.

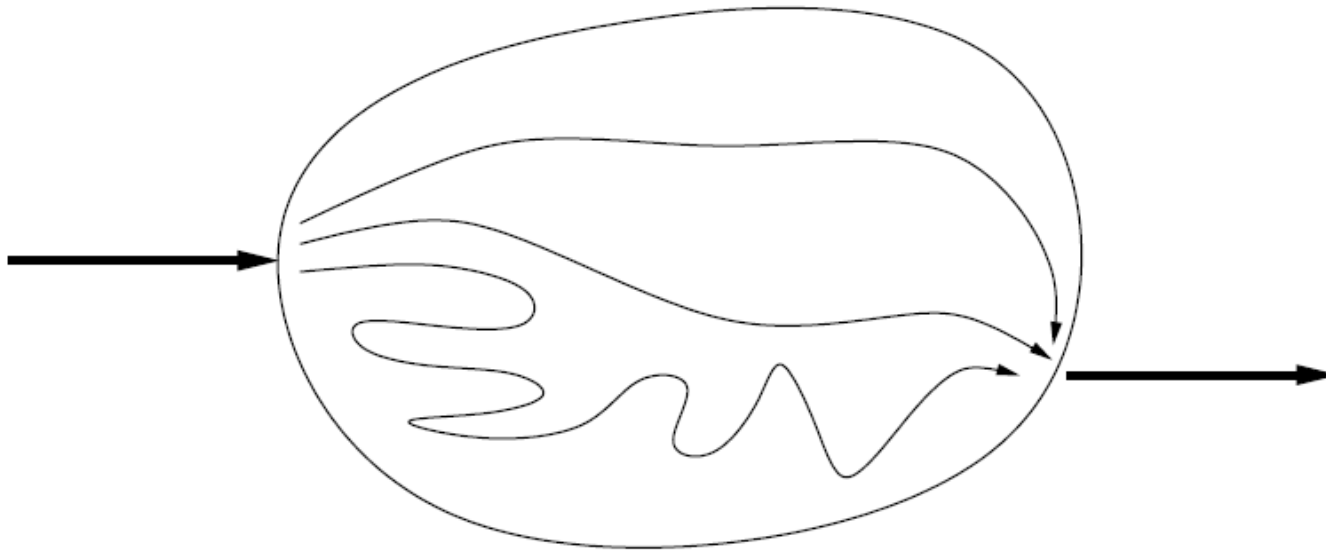
- Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel.



- **If we know precisely what is happening within the vessel, thus if we have a complete velocity distribution map for the fluid in the vessel, then we should, in principle, be able to predict the behavior of a vessel as a reactor. Unfortunately, this approach is impractical, even in today's computer age.**

Residence-Time Distribution : Definition

- Consider an arbitrary reactor with single feed and effluent streams depicted in the following figure



- Without solving for the entire flow field, which might be quite complex, we would like to characterize the flow pattern established in the reactor at steady state.
- The residence-time distribution (RTD) of the reactor is one such characterization or measure of the flow pattern.

- Imagine we could slip some inert tracer molecules into the feed stream and could query these molecules on their exit from the reactor as to how much time they had spent in the reactor.

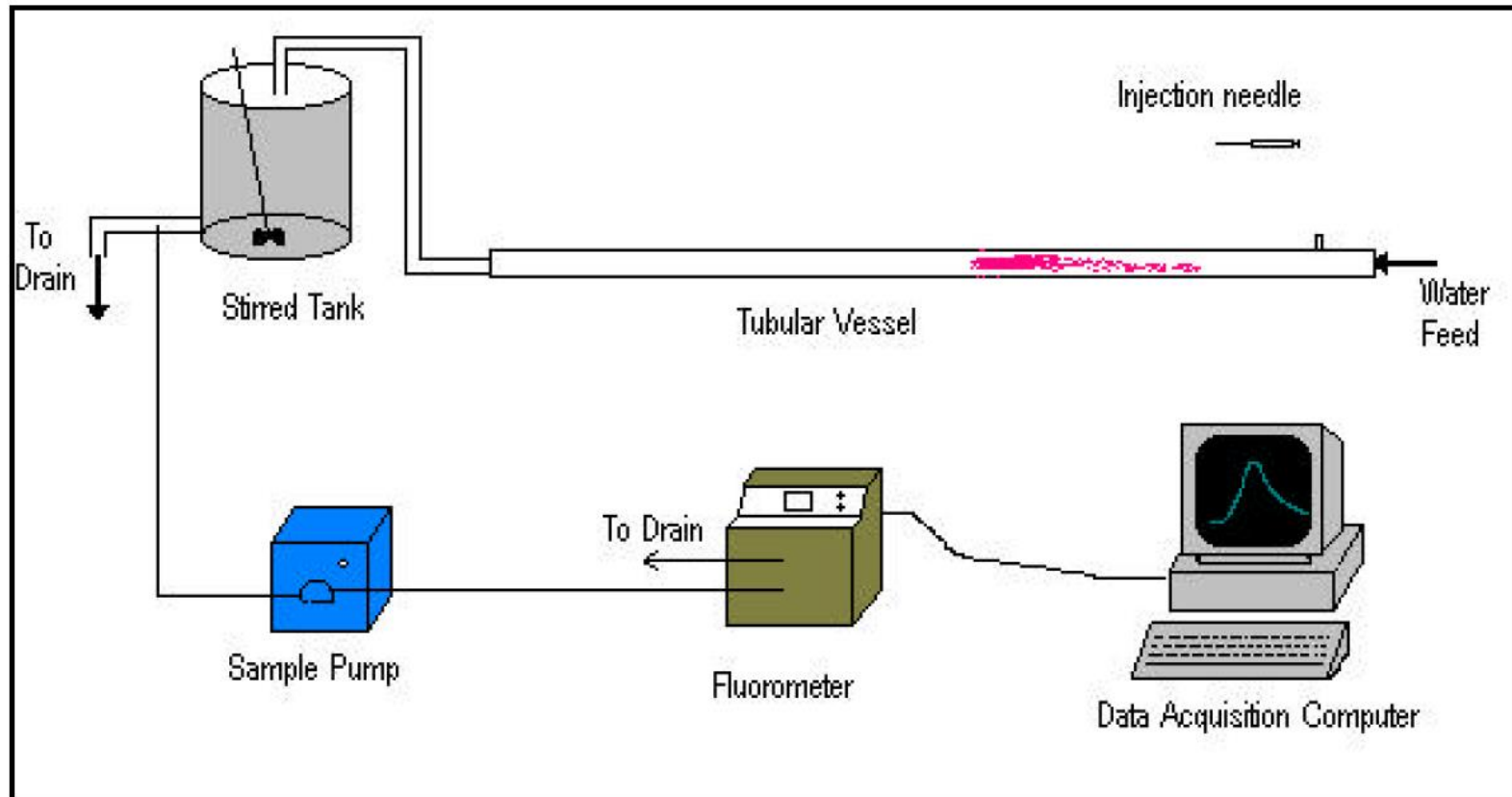
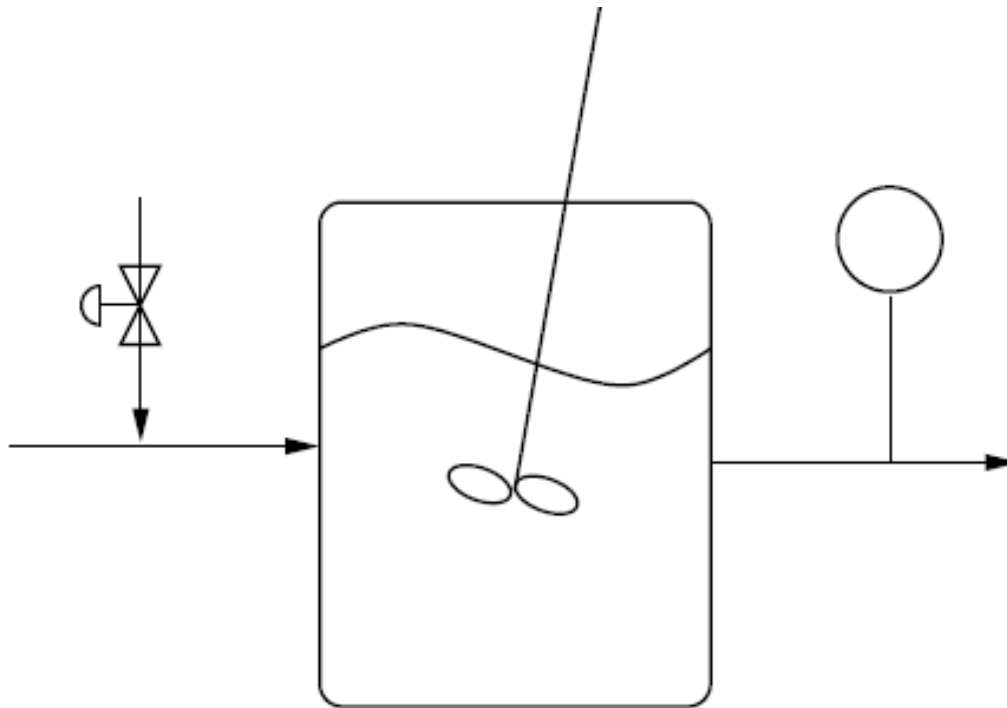


Figure 1 - RTD Experimental Setup

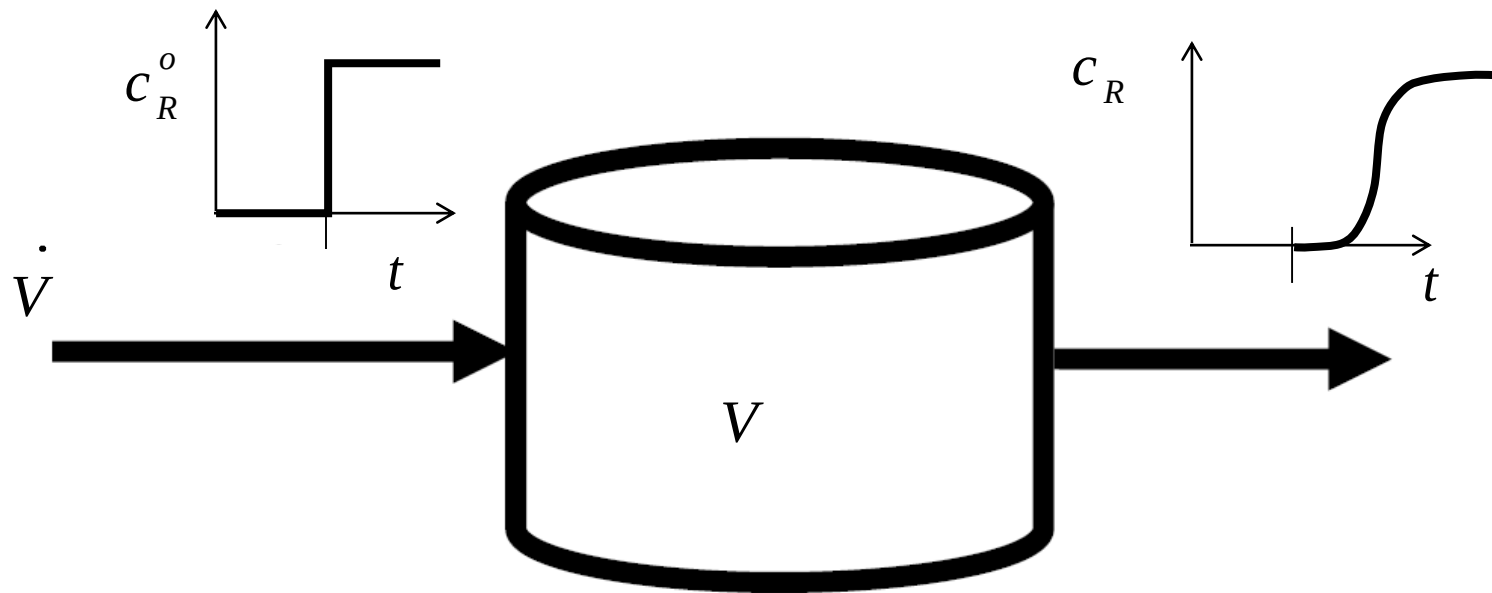
- **Some of the tracer molecules might happen to move in a very direct path to the exit; some molecules might spend a long time in a poorly mixed zone before finally ending their way to the exit.**
- **Due to their random motions as well as convection with the established flow, which itself might be turbulent, we would start recording a distribution of residence times and we would create the residence-time probability density or residence-time distribution.**
- **If the reactor is at steady state, and after we had collected sufficient residence-time statistics, we expect the residence-time distribution to also settle down to a steady function.**

Continuous-stirred-tank reactor - CSTR

We next examine again the well-stirred reactor.



- Consider the following step-response experiment: a clear fluid with flowrate $\dot{V}$ enters a well-stirred reactor of volume V
- At time zero we start adding a small flow of a tracer to the feed stream and measure the tracer concentration in the effluent stream.
- We expect to see a continuous change in the concentration of the effluent stream until, after a long time, it matches the concentration of the feed stream.



- Assuming constant density, the differential equation governing the balance of red dye, c_R , in the reactor follows from equation

$$V_R \frac{dc_R}{dt} = \dot{V} (c_R^o - c_R)$$

$$t = 0, c_R = 0$$

- We introduce average residence time

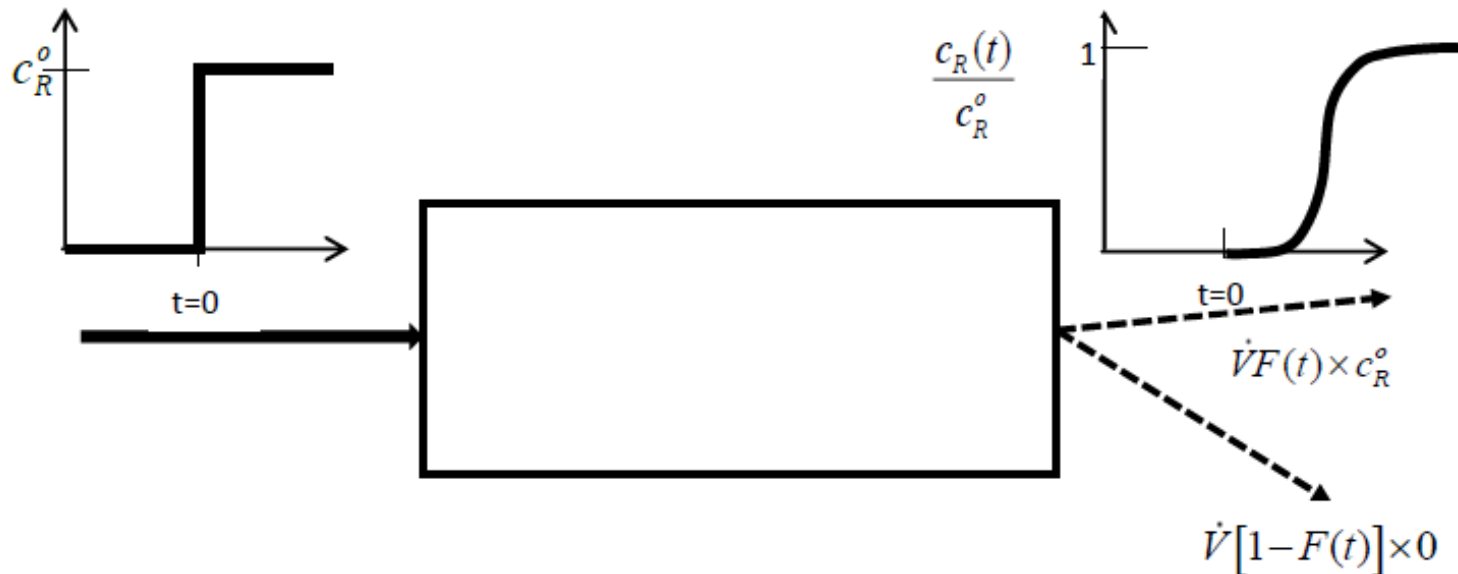
$$\bar{\tau} = \frac{V}{\dot{V}}$$

- Solution of red color dye balance becomes

$$c_R(t) = c_R^o \left(1 - e^{-\frac{t}{\bar{\tau}}} \right)$$

Cumulative Residence Time Distribution function (F – function)

$F(\tau)$ – The fraction of fluid of the effluent stream which has been in the reactor time less than τ



$$\dot{V}c_R(t) = \dot{V} [1 - F_{CSTR}(t)] \times 0 + \dot{V}F_{CSTR}(t) \times c_R^o$$

$$F_{CSTR}(\tau) = \frac{c_R(\tau)}{c_R^o} = 1 - e^{-\frac{\tau}{\bar{\tau}}}$$

Residence Time Distribution (RTD) function (E– function)

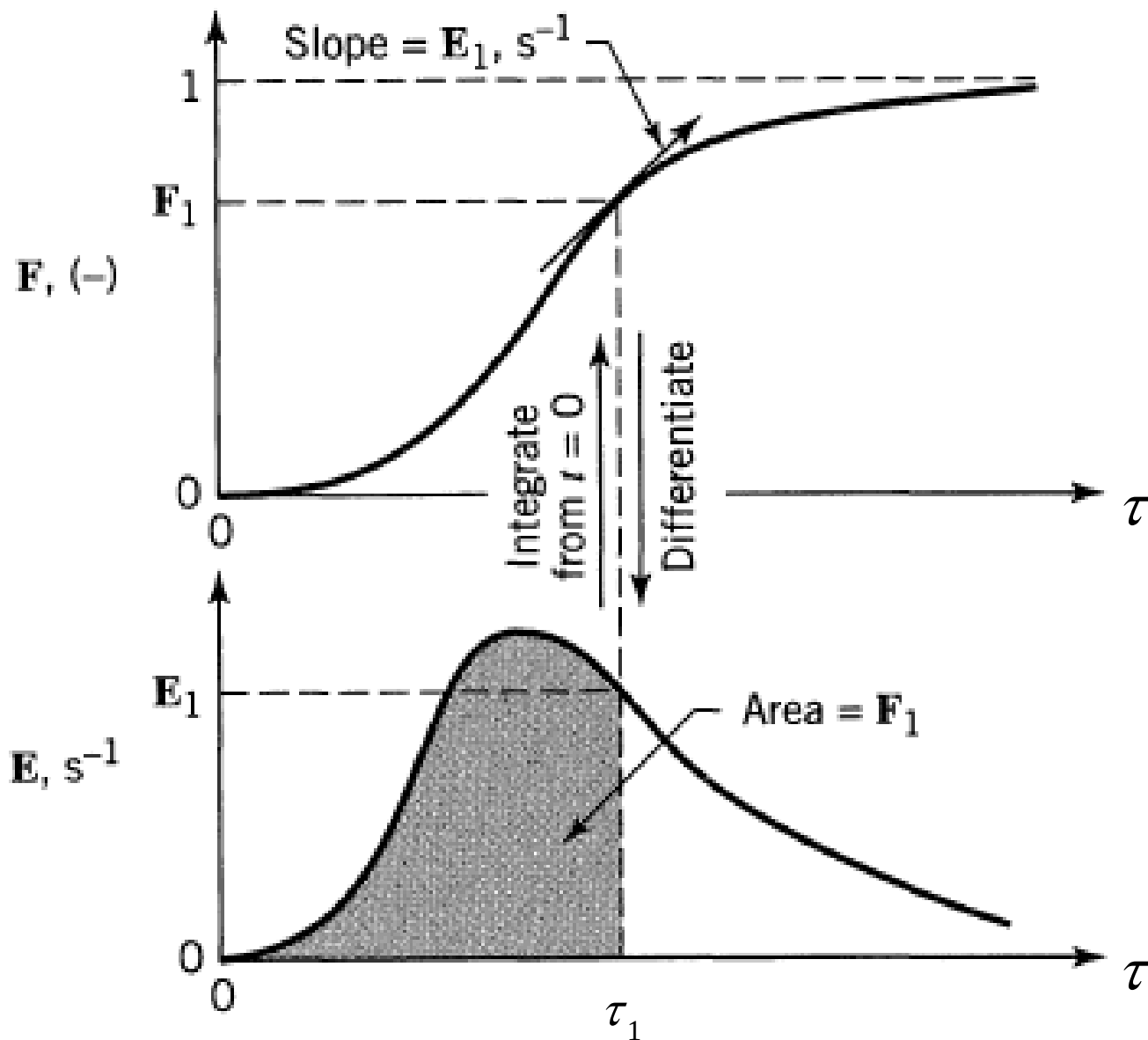
$E(\tau)$ – The fraction of fluid of the effluent stream which has been in the reactor in time interval $(\tau ; \tau + d\tau)$

$$E(\tau) = \frac{dF}{d\tau}$$

$$E_{CSTR}(\tau) = \frac{1}{\bar{\tau}} e^{-\frac{\tau}{\bar{\tau}}}$$

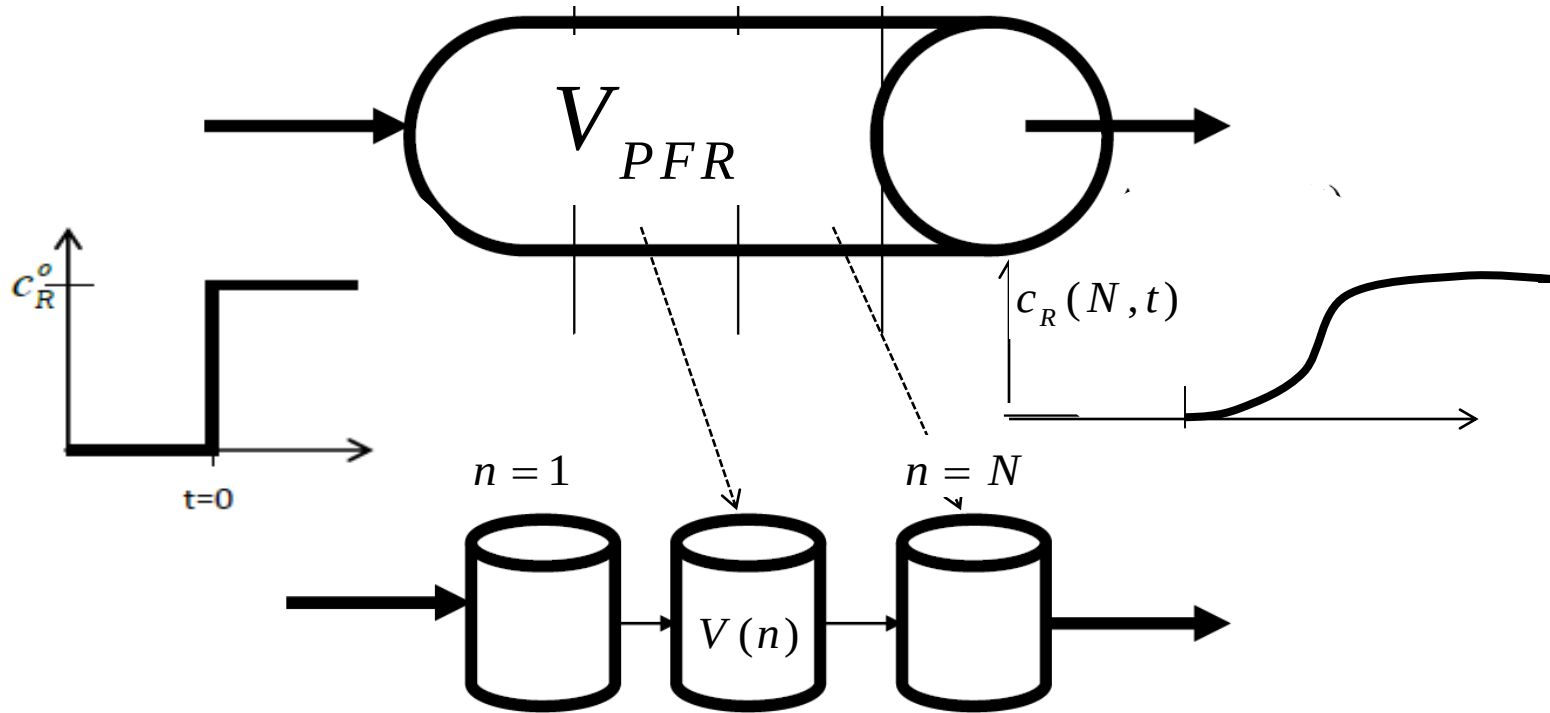
Mean Residence Time

$$\tau_{mean} = \int_0^{\infty} \tau E(\tau) d\tau = \int_0^{\infty} \frac{\tau}{\bar{\tau}} e^{-\frac{\tau}{\bar{\tau}}} d\tau = \bar{\tau}$$



Relationship between the $E(\tau)$ and $F(\tau)$ functions

Plug flow reactor can be represented by a cascade of small CSTR



$$V(n) = \frac{V_{PFR}}{N}, \bar{\tau}(n) = \frac{V(n)}{\dot{V}} = \frac{V_{PFR}}{N\dot{V}} = \frac{\bar{\tau}}{N}$$

$$V(n) \frac{dc_R(n, t)}{dt} = \dot{V} (c_R(n-1, t) - c_R(n, t))$$

$$\frac{dc_R(n, t)}{dt} = \frac{N}{\bar{\tau}} (c_R(n-1, t) - c_R(n, t))$$

$$n = 1, 2, \dots, N$$

With the initial condition , the solution becomes (integration of linear differential equation by integrating factor):

$$c_R(n, t) = \frac{N}{\bar{\tau}} e^{-\frac{Nt}{\bar{\tau}}} \int_0^t c_R(n-1, y) e^{\frac{Ny}{\bar{\tau}}} dy$$

Calculation of the integral for the first reactor where

$$c_R(n-1, t) = c_R^o = \text{constant}$$

and then for the successive ones yields the final result:

$$\frac{c_R(N, t)}{c_R^o} = F_N(t) = 1 - e^{-\frac{Nt}{\bar{\tau}}} \left[1 + \frac{Nt}{\bar{\tau}} + \frac{1}{2!} \left(\frac{Nt}{\bar{\tau}} \right)^2 + \dots + \frac{1}{(N-1)!} \left(\frac{Nt}{\bar{\tau}} \right)^{N-1} \right]$$

$$F_N(\tau) = 1 - e^{-\frac{N\tau}{\bar{\tau}}} \sum_{j=1}^N \frac{1}{(j-1)!} \left(\frac{N\tau}{\bar{\tau}} \right)^{j-1}$$

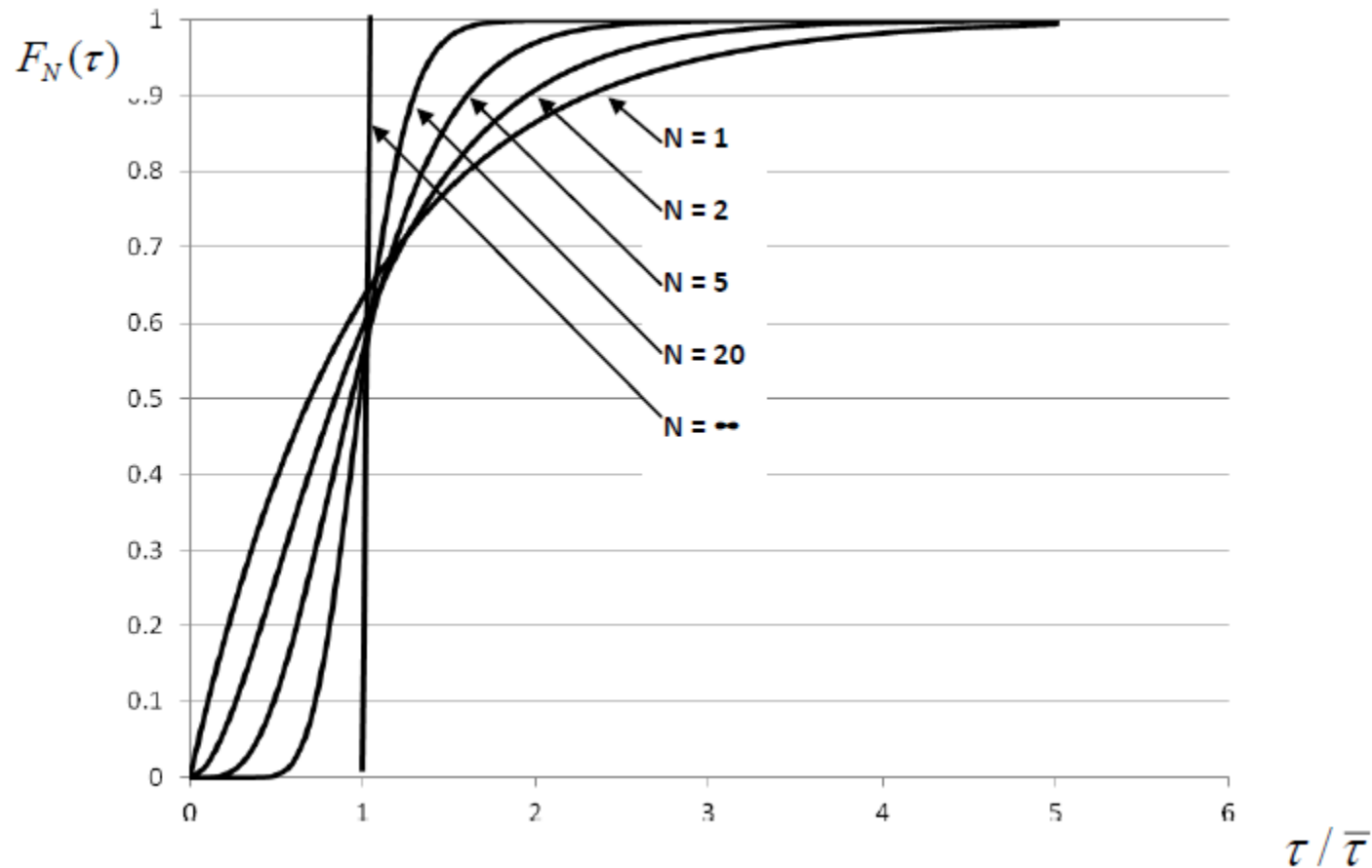


Fig. Cumulative residence time distribution $F_N(\tau)$ curves for several cascades of N equal CSTR reactors.

If the $E(\tau)$ function is calculated, we obtain

$$\begin{aligned}
 E_N(\tau) &= \frac{F_N(\tau)}{d\tau} = \frac{d}{d\tau} \left\{ 1 - e^{-\frac{N\tau}{\bar{\tau}}} \sum_{j=1}^N \frac{1}{(j-1)!} \left(\frac{N\tau}{\bar{\tau}} \right)^{j-1} \right\} = \\
 &= \frac{N}{\bar{\tau}} e^{-\frac{N\tau}{\bar{\tau}}} \sum_{j=1}^N \frac{1}{(j-1)!} \left(\frac{N\tau}{\bar{\tau}} \right)^{j-1} - e^{-\frac{N\tau}{\bar{\tau}}} \frac{N}{\bar{\tau}} \sum_{j=2}^N \frac{1}{(j-2)!} \left(\frac{N\tau}{\bar{\tau}} \right)^{j-2} = \\
 &= \frac{N}{(N-1)!} \frac{1}{\bar{\tau}} \left(\frac{N\tau}{\bar{\tau}} \right)^{N-1} e^{-\frac{N\tau}{\bar{\tau}}}
 \end{aligned}$$

The last equation is called the Poisson distribution function (see figure presented on the next slide).

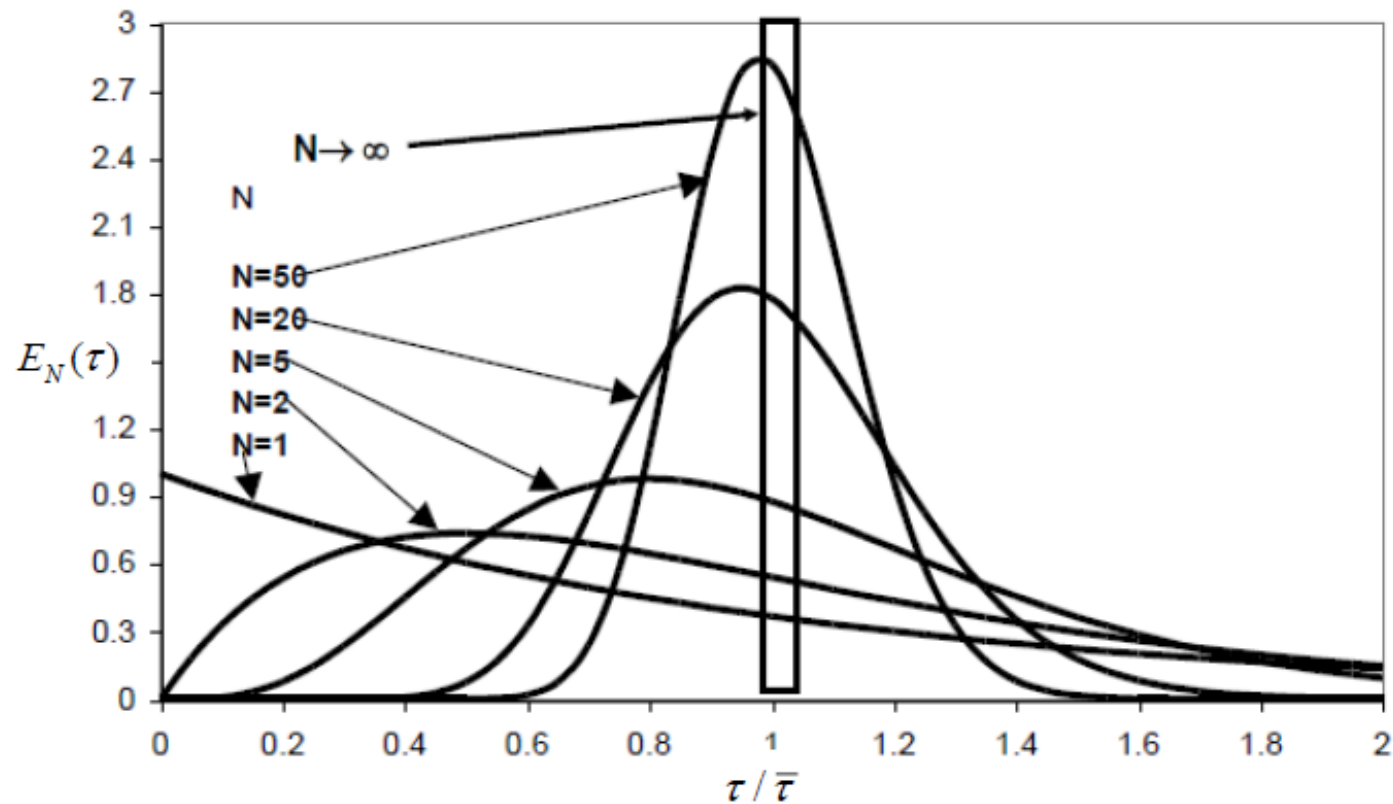


Fig. Residence time distribution $E_N(\tau)$ curves for several cascades of N equal CSTR reactors.

If the slope of the $F(\tau)$ curves is calculated from $E(\tau)$ function near the inflection point (i.e. at $\tau = \bar{\tau}$), we find that it is given by

$$E_N(\bar{\tau}) = \frac{N^{N+1}}{N!} \frac{e^{-N}}{\bar{\tau}}$$

Now, according to the Stirling's rule we have for $N > 5$ within error of 2 % (see Annexe 1)

$$N! \cong \sqrt{2N\pi} N^N e^{-N}$$

Introduction of this approximation into the former equation yields:

$$E_N(\bar{\tau}) = \frac{N^{N+1}}{\sqrt{2N\pi} N^N e^{-N}} \frac{e^{-N}}{\bar{\tau}} = \frac{1}{\bar{\tau}} \sqrt{\frac{N}{2\pi}}$$

This result also illustrates the fact that the $F(\tau)$ curve becomes steeper as N increases.

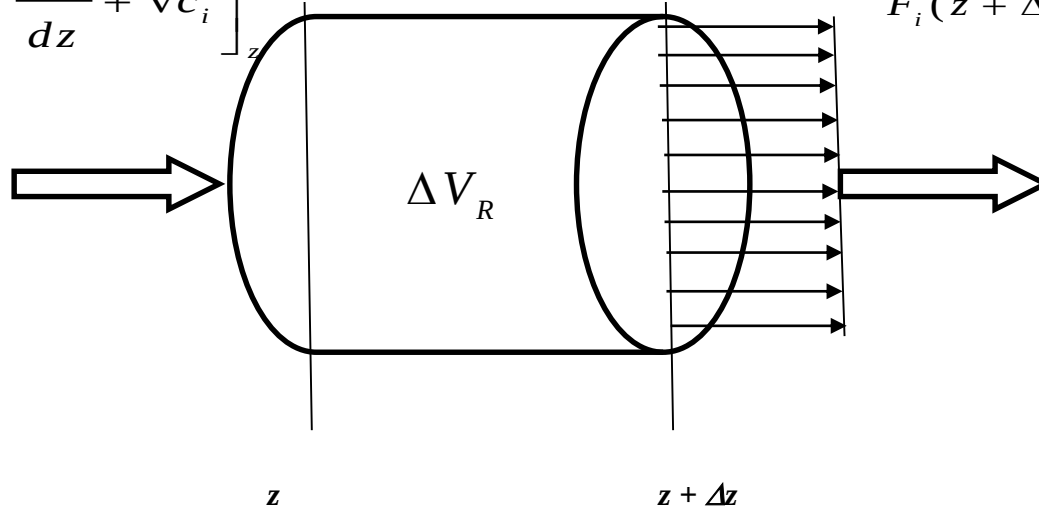
Plug flow reactor can be represented also by a dispersion model

inlet flux of i-th species

$$F_i(z) = S \left[-D_i \frac{dc_i}{dz} + \bar{v} c_i \right]_z$$

outlet flux of i-th species

$$F_i(z + \Delta z) = S \left[-D_i \frac{dc_i}{dz} + \bar{v} c_i \right]_{z + \Delta z}$$

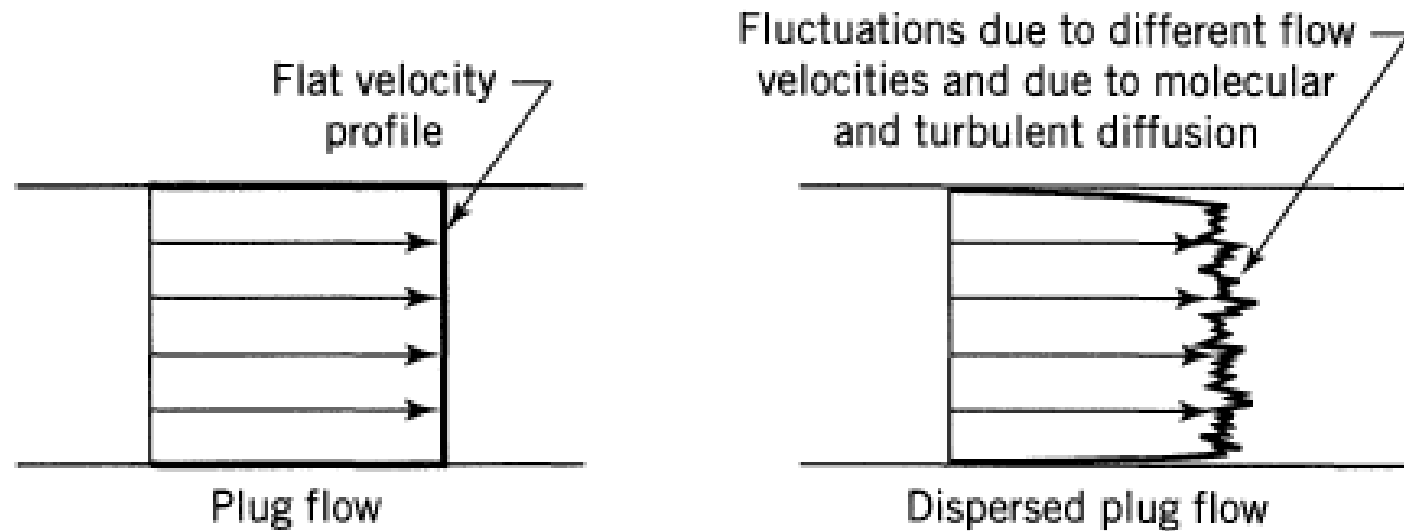


Balance of red component in the volume becomes

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial z^2} - \bar{v} \frac{\partial c_R}{\partial z}$$

D_R is a " dispersion coefficient " which must be determined experimentally

Representation of the dispersion (dispersed plug flow) model.



Together with boundary

$$z = 0, -D_R \frac{\partial c_R}{\partial z} + \bar{v} c_R = \bar{v} c_R^o$$

$$z = L, D_R \frac{\partial c_R}{\partial z} = 0$$

and initial conditions

$$t = 0, 0 < z \leq L, c_R = 0$$

Outlet concentration of red component is given by (see Annexe 2)

$$c_R(L, t) = \frac{c_R^o}{2} \left[1 - \operatorname{erf} \left(\frac{L - \bar{v}t}{\sqrt{4D_R t}} \right) \right] =$$

$$= \frac{c_R^o}{2} \left[1 - \operatorname{erf} \left(\frac{1 - t / \bar{\tau}}{\sqrt{4t / (Pe \cdot \bar{\tau})}} \right) \right]$$

$$\bar{\tau} = \frac{V_R}{\bar{v}} = \frac{L}{\bar{v}}, Pe = \frac{L \bar{v}}{D_R}$$

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp[-y^2] dy$$

Therefore the cumulative residence time distribution $F_N(\tau)$ curves for PFR with dispersion are given by

$$F_{PFR}(\tau) = \frac{c_R(L, \tau)}{c_R^o} = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{1 - \tau / \bar{\tau}}{\sqrt{4\tau / (Pe \cdot \bar{\tau})}} \right) \right]$$

$$\bar{\tau} = \frac{V_R}{\bar{V}} = \frac{L}{\bar{V}}, Pe = \frac{L \bar{V}}{D_R}$$

$$F_{PFR} = \frac{c_R(L, t)}{c_R^o}$$

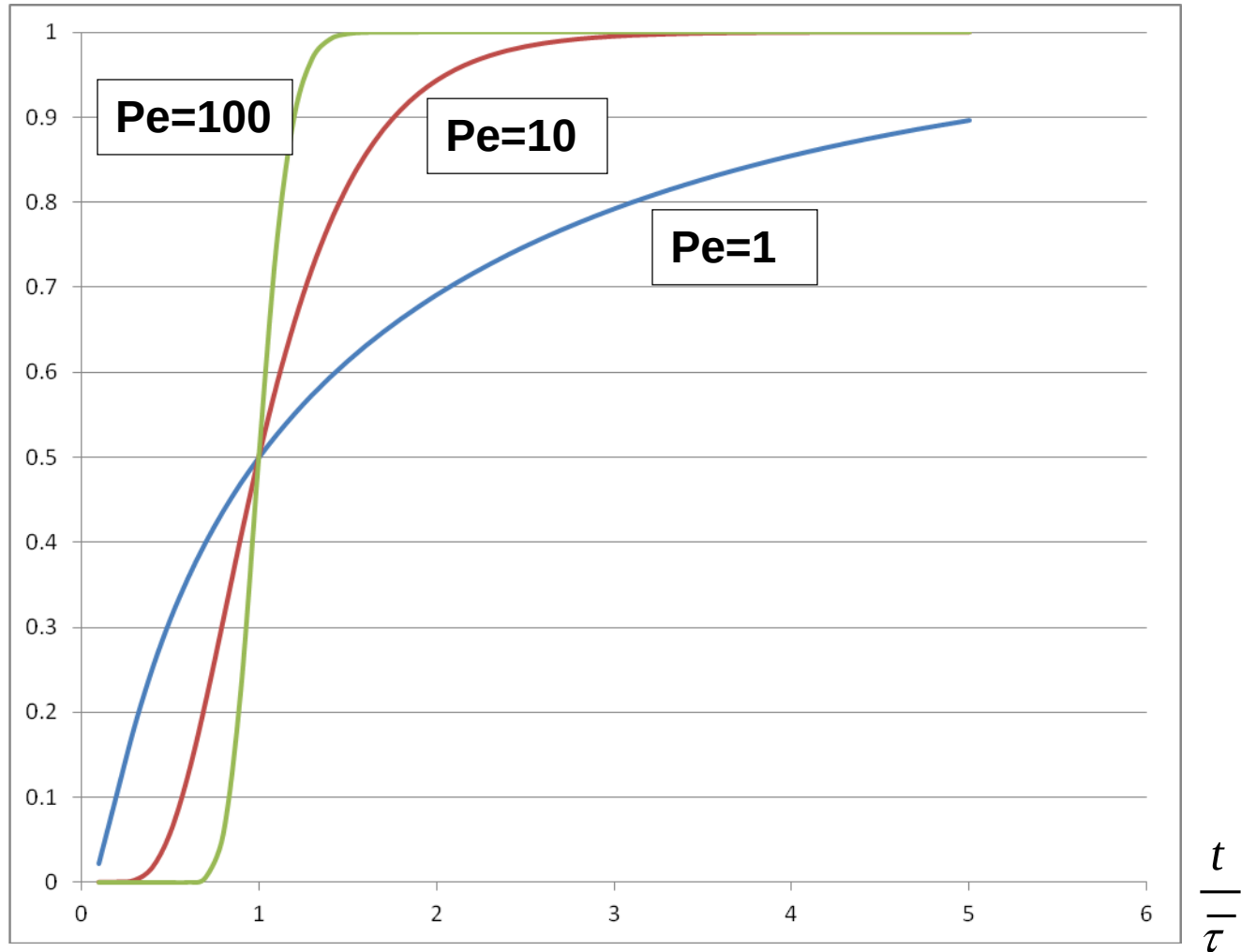


Fig. Cumulative residence time distribution $F_{PFR}(\tau)$ curves for PFR with dispersion

We can differentiate $F_{PFR}(\tau)$ equation to obtain the curve for dispersed plug-flow Residence Time Distribution

$$E_{PFR}(\tau) = \frac{dF_{PFR}(\tau)}{d\tau} = \frac{\sqrt{Pe}}{4\bar{\tau}\sqrt{\pi}} \left(\frac{\bar{\tau}/\tau + 1}{\sqrt{\tau/\bar{\tau}}} \right) \exp \left[- \left(\frac{1 - \tau/\bar{\tau}}{\sqrt{4\tau/(Pe.\bar{\tau})}} \right)^2 \right] \cong$$

$$\cong \frac{1}{2} \sqrt{\frac{Pe}{\pi\tau\bar{\tau}}} \exp \left[- \left(\frac{1 - \tau/\bar{\tau}}{\sqrt{4\tau/(Pe.\bar{\tau})}} \right)^2 \right]$$

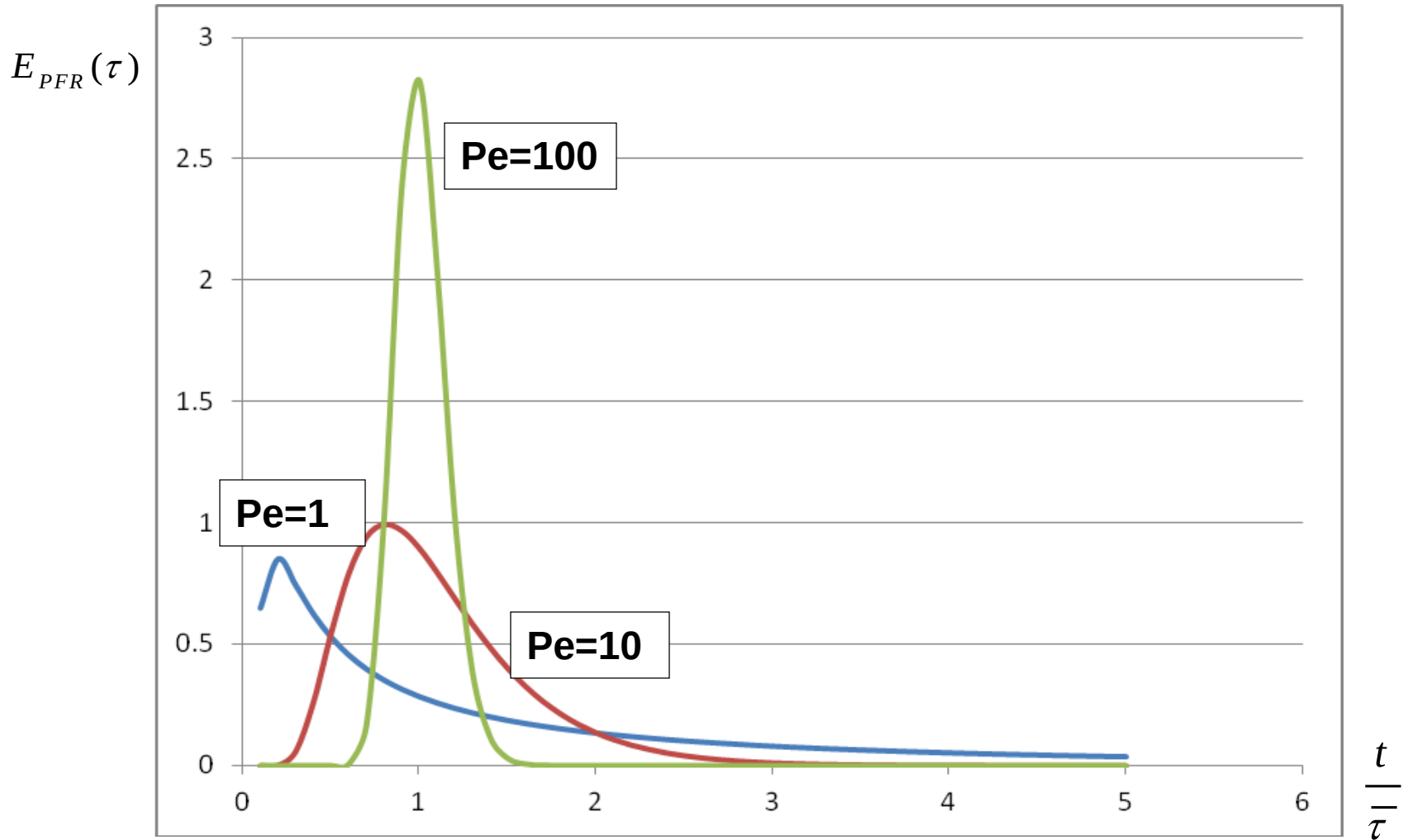
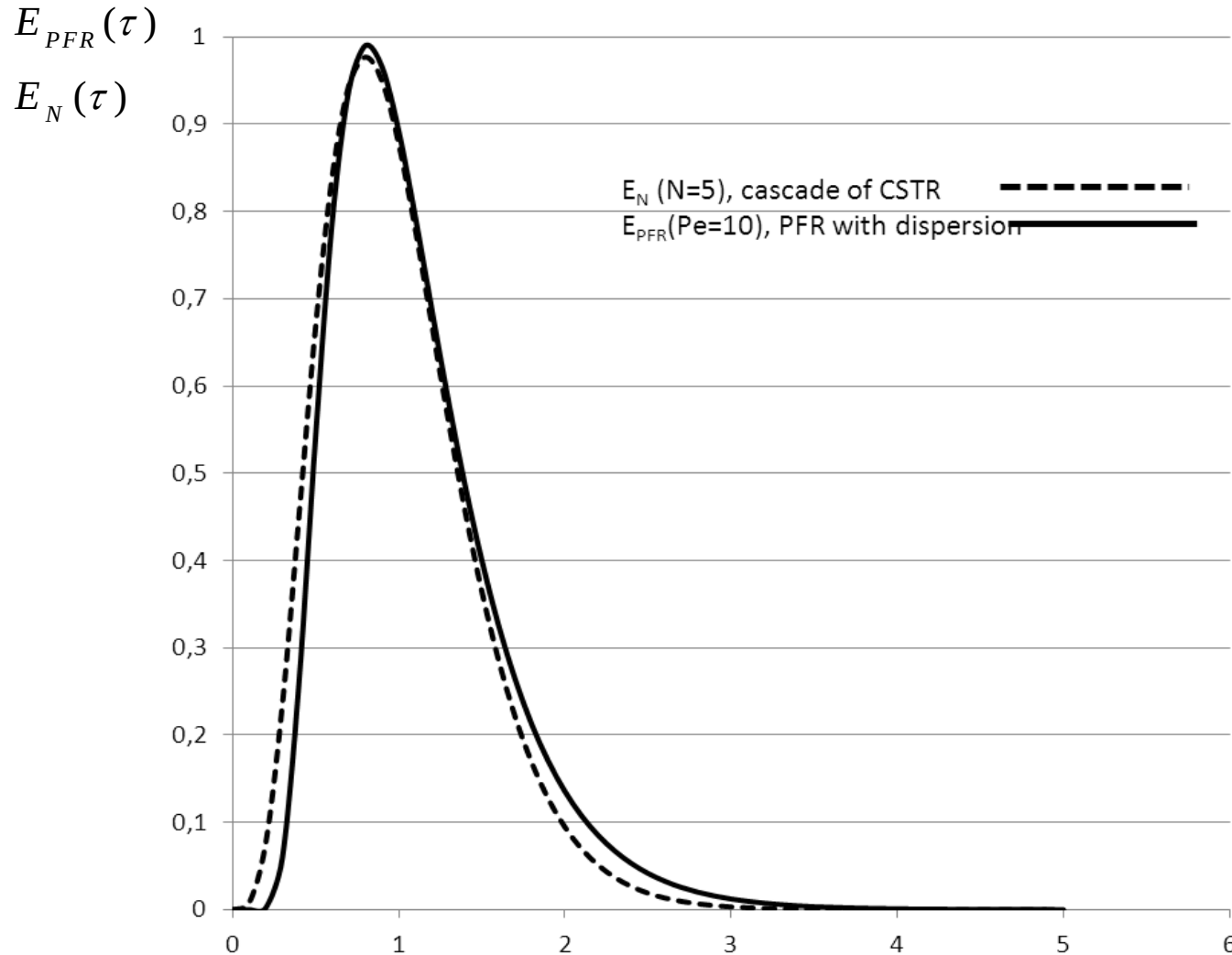


Fig. Residence time distribution $E_{PFR}(\tau)$ curves for PFR with dispersion

Comparison of the cascade and the dispersion models

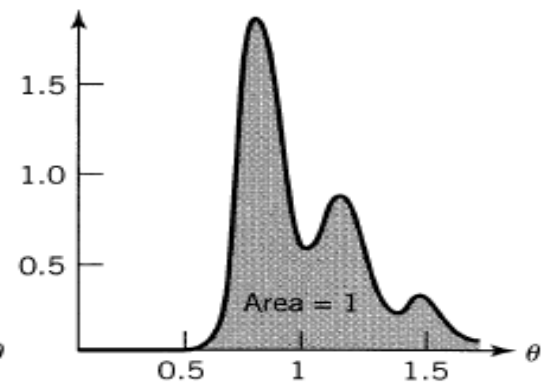
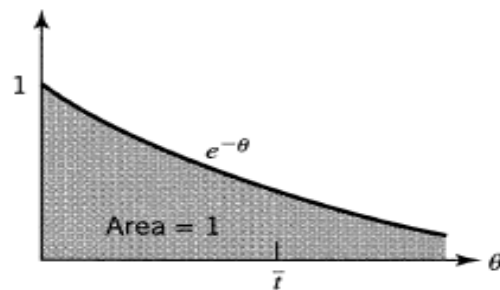
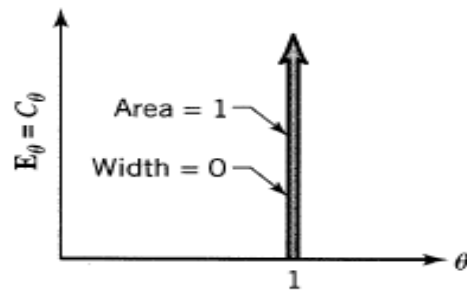
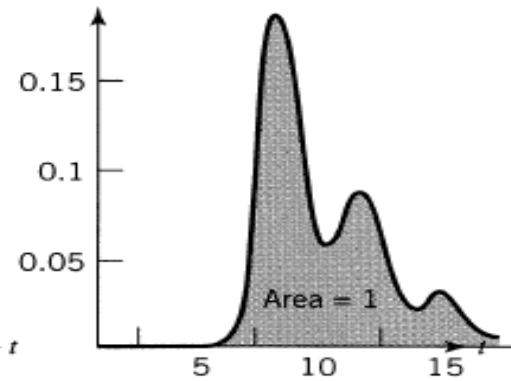
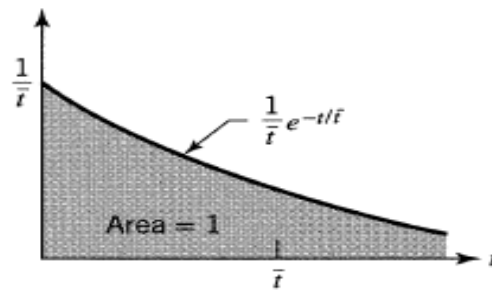
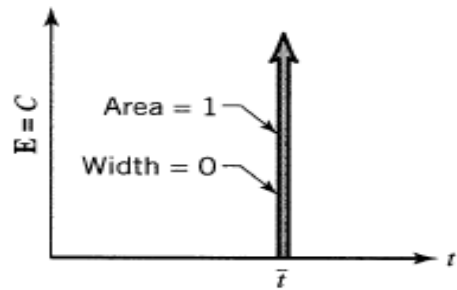
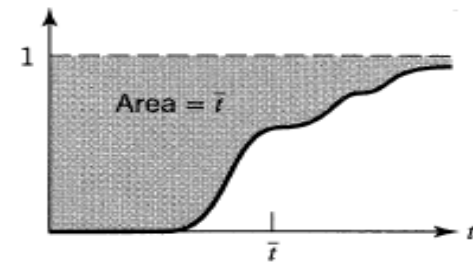
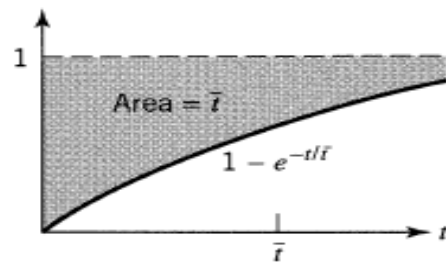
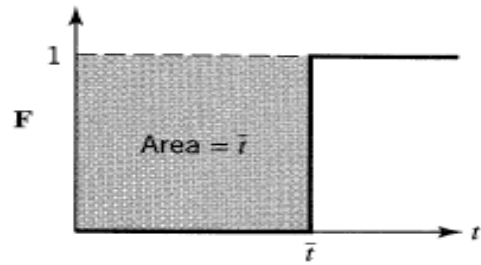
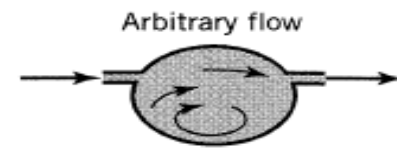
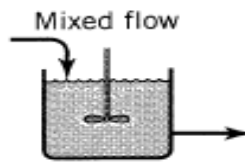
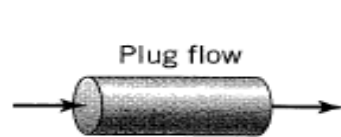


$$E_{PFR}(\bar{\tau}) \cong E_N(\bar{\tau})$$

$$\frac{\sqrt{Pe}}{2\bar{\tau}\sqrt{\pi}} = \frac{1}{\bar{\tau}}\sqrt{\frac{N}{2\pi}}$$

$$\frac{Pe}{2} = N$$

$$\frac{t}{\tau}$$



1-D pseudo homogenous model with axial dispersion

$$\frac{1}{Pe_A} \frac{d^2 Y_A}{dx^2} - \frac{dY_A}{dx} - Da_A Y_A = 0$$

$$x = 0 \quad \frac{1}{Pe_A} \frac{dY_A}{dx} = Y_A - 1$$

$$x = 1 \quad \frac{dY_A}{dx} = 0$$

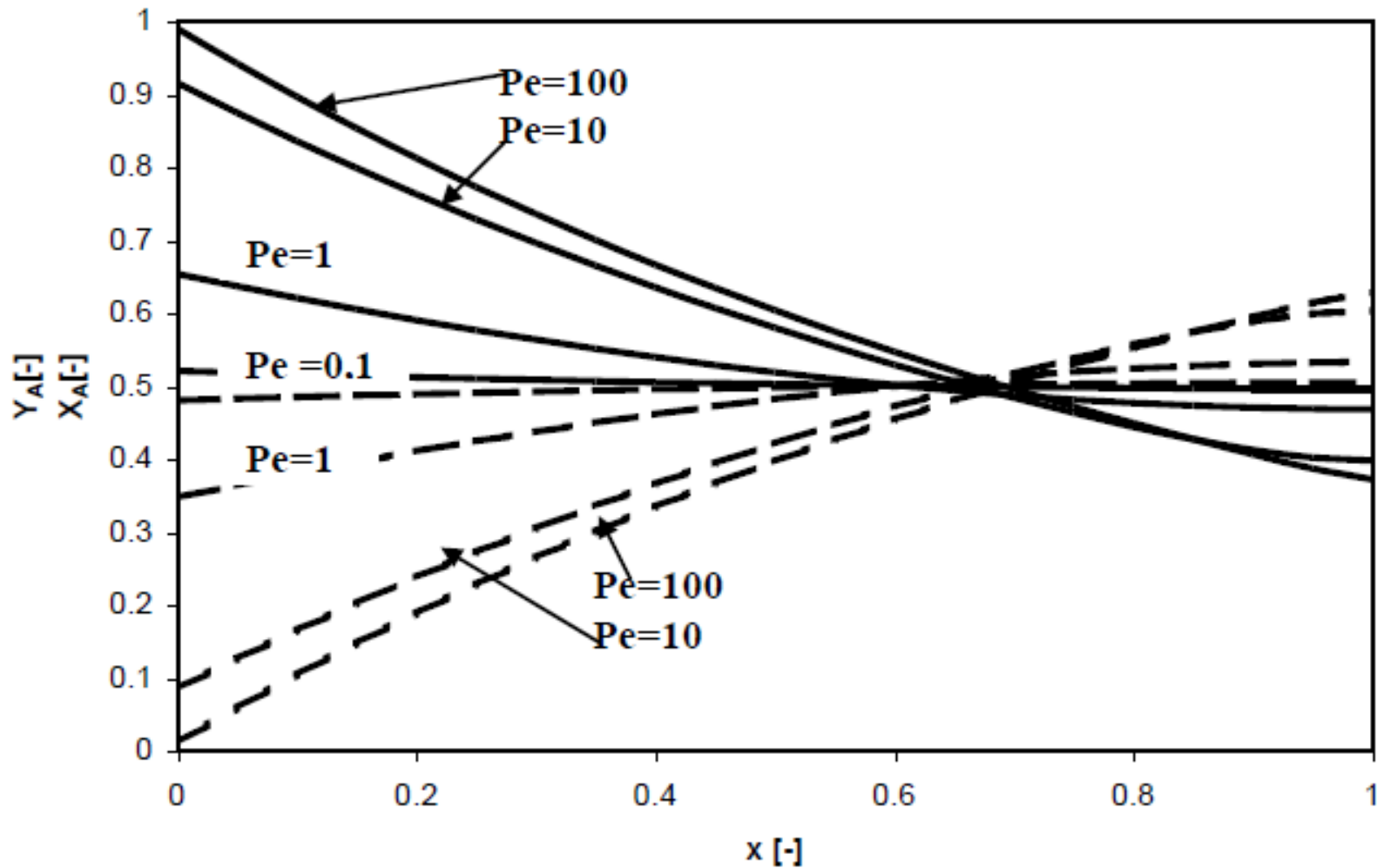
$$x = \frac{z}{L}$$

$$Y_A = \frac{c_A}{c_A^o} \quad Pe_A = \frac{\bar{v}L}{D_A} \quad Da_A = \frac{kL}{\bar{v}}$$

To calculate

a) $Y_A(x)$

b) Conversion(x) = $X_A(x) = 1 - Y_A(x)$ for various values of Pe



$Y_A(x)$ (solid lines) and $X_A(x)$ (dashed lines) in isothermal reactor with axial dispersion and 1st order kinetics

Annexe 1

Stirling's formula

There exists an approximation due to Stirling (James Stirling, British mathematician (1692-1770)), which is very useful in the evaluation of factorials of large numbers. It can be derived in several ways. For example, the Gamma function is defined by

$$\Gamma(x) = \int_0^{\infty} t^{x-1} e^{-t} dt$$

If x is replaced by $n + 1$, a positive integer, $\Gamma(x)$ becomes

$$\Gamma(n+1) = n! = \int_0^{\infty} t^n e^{-t} dt = \int_0^{\infty} e^{n \ln t - t} dt$$

The function $e^{n \ln t - t}$ has a sharp maximum at $t = n$ where $p(t) = n \ln t - t$ has maximum, too. We can develop function $p(t) = n \ln t - t$ at $t = n$ using Taylor's series:

$$\begin{aligned} p(t) &= n \ln t - t = p(n) + \frac{p'(n)}{1!} (t-n) + \frac{p''(n)}{2!} (t-n)^2 + \frac{p'''(n)}{3!} (t-n)^3 + \dots = \\ &= n \ln n - n - \frac{1}{2!} \left(\frac{t-n}{\sqrt{n}} \right)^2 + \dots \end{aligned}$$

Thus $\Gamma(n+1)$ becomes

$$\begin{aligned} \Gamma(n+1) &= n! \cong \int_0^{\infty} \exp \left[n \ln(n) - n - \frac{1}{2!} \left(\frac{t-n}{\sqrt{n}} \right)^2 \right] dt = n^n e^{-n} \sqrt{2n} \int_{-\sqrt{n/2}}^{\infty} e^{-y^2} dy \cong \\ &\cong \sqrt{2n\pi} n^n e^{-n} = \sqrt{2n\pi} \left(\frac{n}{e} \right)^n \end{aligned}$$

because $\int_{-\sqrt{n/2}}^{\infty} e^{-y^2} dy \cong \sqrt{\pi}$ for large n .

The accuracy of Stirling's formula is confirmed for large n in the table below:

n	n!	Stirling	rel. error, %
2	2	1.919004351	4.049782
10	3628800	3598695.619	0.829596
20	2.4329E+18	2.42279E+18	0.415765
50	3.0414E+64	3.03634E+64	0.166526
100	9.3326E+157	9.3248E+157	0.083298

Annexe 2

Balance of red component in the volume ΔV_R becomes

$$\frac{\partial c_R}{\partial t} - D_R \frac{\partial^2 c_R}{\partial z^2} - v \frac{\partial c_R}{\partial z}$$

together with boundary conditions

$$z = 0 : -D_R \frac{\partial c_R}{\partial z} + \bar{v} c_R = \bar{v} c_R^0$$

$$z = L : D_R \frac{\partial c_R}{\partial z} = 0$$

and initial conditions

$$t = 0, 0 < z \leq L, c_R = 0$$

D_R is a "dispersion coefficient" which must be determined experimentally.

Using transformed variables

$$x = x(z, t) = z - vt$$

$$\theta = \theta(z, t) = t$$

we obtain

$$\frac{\partial c_R}{\partial t} = \frac{\partial c_R}{\partial \theta} \frac{\partial \theta}{\partial t} + \frac{\partial c_R}{\partial x} \frac{\partial x}{\partial t} = \frac{\partial c_R}{\partial \theta} - v \frac{\partial c_R}{\partial x}$$

$$\frac{\partial c_R}{\partial z} = \frac{\partial c_R}{\partial \theta} \frac{\partial \theta}{\partial z} + \frac{\partial c_R}{\partial x} \frac{\partial x}{\partial z} = \frac{\partial c_R}{\partial x}$$

$$\frac{\partial^2 c_R}{\partial z^2} = \frac{\partial^2 c_R}{\partial x^2}$$

$$\frac{\partial c_R}{\partial \theta} - D_R \frac{\partial^2 c_R}{\partial x^2}$$

$$x > 0, \theta = 0, c_R = 0$$

$$x < 0, \theta = 0, c_R = c_R^0$$

$$x \rightarrow \infty, \theta > 0, c_R \rightarrow 0$$

$$x \rightarrow -\infty, \theta > 0, c_R \rightarrow c_R^0$$

This equation can be solved by Boltzmann transformation

$$u = \frac{x}{\sqrt{4D_R\theta}}$$

$$\begin{aligned}\frac{\partial c_R}{\partial \theta} - \frac{dc_R}{du} \frac{\partial u}{\partial \theta} &= -\frac{1}{2} \frac{x}{\sqrt{4D_R \theta}} \frac{1}{\theta} \frac{dc_R}{du} = -\frac{1}{2} \frac{u}{\theta} \frac{dc_R}{du} \\ \frac{\partial c_R}{\partial x} - \frac{dc_R}{du} \frac{\partial u}{\partial x} &= \frac{1}{\sqrt{4D_R \theta}} \frac{dc_R}{du} \\ \frac{\partial^2 c_R}{\partial x^2} &= \frac{1}{4D_R \theta} \frac{d^2 c_R}{du^2}\end{aligned}$$

And we have finally

$$\frac{d^2 c_R}{du^2} + 2u \frac{dc_R}{du} = 0$$

Boundary and initial conditions become

$$u \rightarrow -\infty, c_R \rightarrow c_R^0$$

$$u \rightarrow \infty, c_R \rightarrow 0$$

After integrating the last equation we have (taking into account $\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi}$)

$$\begin{aligned}\frac{dc_R}{du} &= B_1 \exp[-u^2] \\ c_R(u) - c_R(-\infty) &= c_R(u) - c_R^0 = B_1 \int_{-\infty}^u \exp[-y^2] dy \\ B_1 &= -\frac{c_R^0}{\sqrt{\pi}} \\ c_R(u) - c_R^0 &= \left[1 - \frac{1}{\sqrt{\pi}} \int_{-\infty}^u \exp[-y^2] dy \right] = \\ &= c_R^0 \left[1 - \frac{1}{\sqrt{\pi}} \left(\frac{\sqrt{\pi}}{2} + \int_0^u \exp[-y^2] dy \right) \right] = \\ &= -\frac{c_R^0}{2} \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u \exp[-y^2] dy \right] = \\ &= -\frac{c_R^0}{2} [1 - \operatorname{erf}(u)] \\ \operatorname{erf}(u) &= \frac{2}{\sqrt{\pi}} \int_0^u \exp[-y^2] dy\end{aligned}$$

Substituting original variables we would obtain

$$c_R(z,t) = \frac{C_R^0}{2} \left[1 - \operatorname{erf} \left(\frac{z - \bar{v}t}{\sqrt{4D_R t}} \right) \right] - \\
= \frac{C_R^0}{2} \left[1 - \operatorname{erf} \left(\frac{z - \bar{v}t}{\sqrt{4D_R t}} \right) \right] - \\
= \frac{C_R^0}{2} \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{z - \bar{v}t}{\sqrt{4D_R t}}} \exp[-y^2] dy \right]$$

Outlet concentration of red component is given by

$$c_R(L,t) = \frac{C_R^0}{2} \left[1 - \operatorname{erf} \left(\frac{L - \bar{v}t}{\sqrt{4D_R t}} \right) \right] - \\
= \frac{C_R^0}{2} \left[1 - \operatorname{erf} \left(\frac{1 - t / \bar{\tau}}{\sqrt{4t / (Pe \cdot \bar{\tau})}} \right) \right] \\
\bar{\tau} = \frac{V}{\bar{v}} = \frac{L}{\bar{v}} \cdot Pe = \frac{L\bar{v}}{D_R}$$

where $\bar{\tau}$ is the average residence time and Pe stands for Peclet number.

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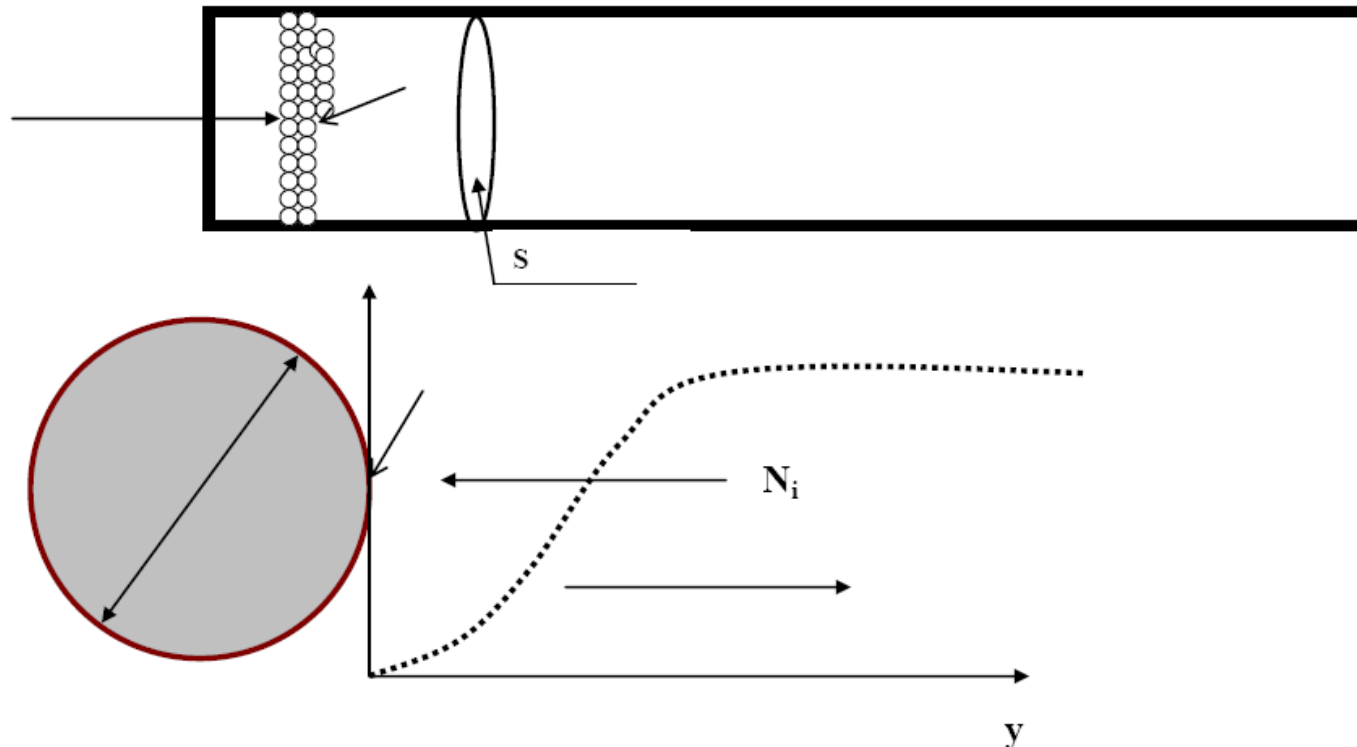
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13. Models of catalytic reactors

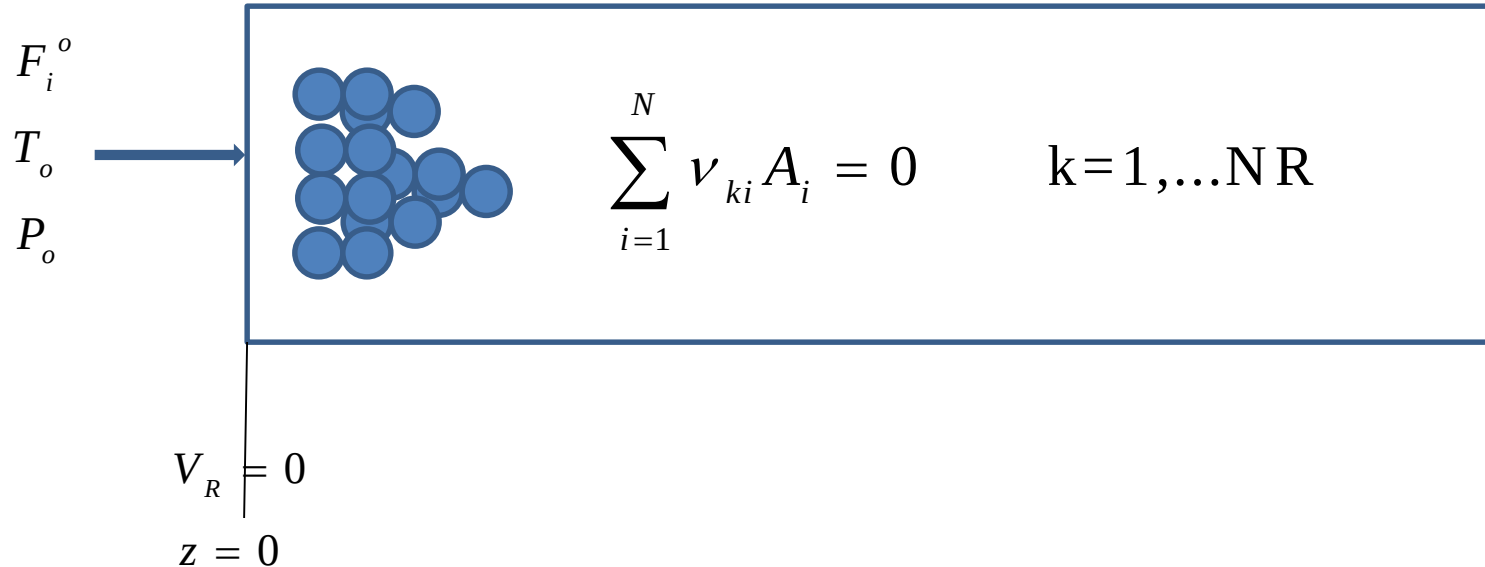
Model equations involve:

- Balance equations for components of reaction mixture in both gas phase and porous catalytical particle
- Balance of energy (enthalpy)
- Balance of momentum
- Flux constitutive equations for component and energy fluxes



	Pseudo homogeneous	Heterogeneous
1-D	• without axial dispersion (pure plug flow) • with axial dispersion	Gradients of concentration and temperature between phases
2-D	Radial dispersion	

1-D pseudo homogeneous model without axial dispersion



We make the following assumptions:

1. Particles of catalyst are small compared to the length of reactor
2. Plug flow in the bed, no radial profiles
3. Neglect axial dispersion in the bed
4. Neglect concentration and temperature gradients in solid catalyst
5. Neglect concentration and temperature gradients in external fluid film
6. Steady state

In the fluid phase, we track the molar flows of all species, the temperature and the pressure. Generally, we can no longer neglect the pressure drop in the tube because of the catalyst bed – Ergun equation.

$$\frac{dF_i}{dz} = S_R \rho_b \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

$$F C_p \frac{dT}{dz} = S_R \left[\rho_b \sum_{k=1}^{NR} (-\Delta_r H_k) r_{M,k} + \frac{4}{d_R} \omega (T_m - T) \right]$$

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

$$z = 0, F_i = F_i^o, T = T_o, P = P_o$$

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)

ρ_b - bed apparent density (kg/m³)

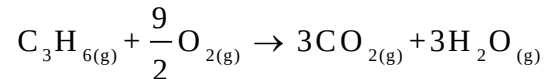
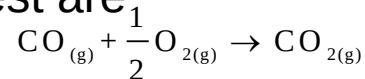
S_R - (empty) reactor cross section area (m²)



Numerical solution
gives $F_i(z), T(z), P(z)$

Example

Consider the oxidation of CO and C₃H₆ in a catalytic converter containing spherical catalyst pellets with particle radius 0.175 cm (0.05 mass % Pt on Al₂O₃). The initial composition of gas mixture is 2 % mol CO, 3 % O₂, 0.05 % C₃H₆ + N₂, total initial molar flow rate is between 0.1 – 2.0 mol/s. Converter has the diameter 10 cm and volume 4.3 litres. Bed porosity is 0.4 and catalyst bed density is 1100 kg/m³. The reactions of interest are



$$r_{M,1} = \frac{k_1(T) c_{\text{O}_2} c_{\text{CO}}}{\left(1 + K_{\text{CO}} c_{\text{CO}} + K_{\text{C}_3\text{H}_6} c_{\text{C}_3\text{H}_6}\right)^2} \quad \text{mol/g/s}$$

$$r_{M,2} = \frac{k_2(T) c_{\text{O}_2} c_{\text{C}_3\text{H}_6}}{\left(1 + K_{\text{CO}} c_{\text{CO}} + K_{\text{C}_3\text{H}_6} c_{\text{C}_3\text{H}_6}\right)^2} \quad \text{mol/g/s}$$

$$k_1(T) = 7.07 \times 10^{19} \exp\left[-\frac{13106}{T}\right] \quad \text{cm}^6/(\text{molgs})$$

$$k_2(T) = 1.47 \times 10^{21} \exp\left[-\frac{15109}{T}\right] \quad \text{cm}^6/(\text{molgs})$$

$$K_{\text{CO}} = 8.099 \times 10^6 \exp\left[\frac{409}{T}\right] \quad \text{cm}^3/\text{mol}$$

$$K_{\text{C}_3\text{H}_6} = 2.579 \times 10^8 \exp\left[-\frac{191}{T}\right] \quad \text{cm}^3/\text{mol}$$

Oh, S.H., Cavenish J.C.,
Hegedus L.L., AICHE J. 26
(1980) 935.

Data from <http://webbook.nist.gov/chemistry/>:

$c_{p,i}(750\text{ K})$:

$$c_{p,CO} = 31.5 \quad \text{J/mol/K} \quad \Delta H_{f,298.15} = -110.53 \text{ kJ/mol}$$

$$c_{p,O_2} = 33.4 \quad \text{J/mol/K}$$

$$c_{p,CO_2} = 50.0 \quad \text{J/mol/K} \quad \Delta H_{f,298.15} = -393.52 \text{ kJ/mol}$$

$$c_{p,N_2} = 31.1 \quad \text{J/mol/K}$$

$$c_{p,C_3H_6} = 123.9 \quad \text{J/mol/K} \quad \Delta H_{f,298.15} = 20.41 \text{ kJ/mol}$$

$$c_{p,H_2O} = 38.12 \quad \text{J/mol/K} \quad \Delta H_{f,298.15} = -241.83 \text{ kJ/mol}$$

Viscosity of $N_{2(g)}$ at 750 K:

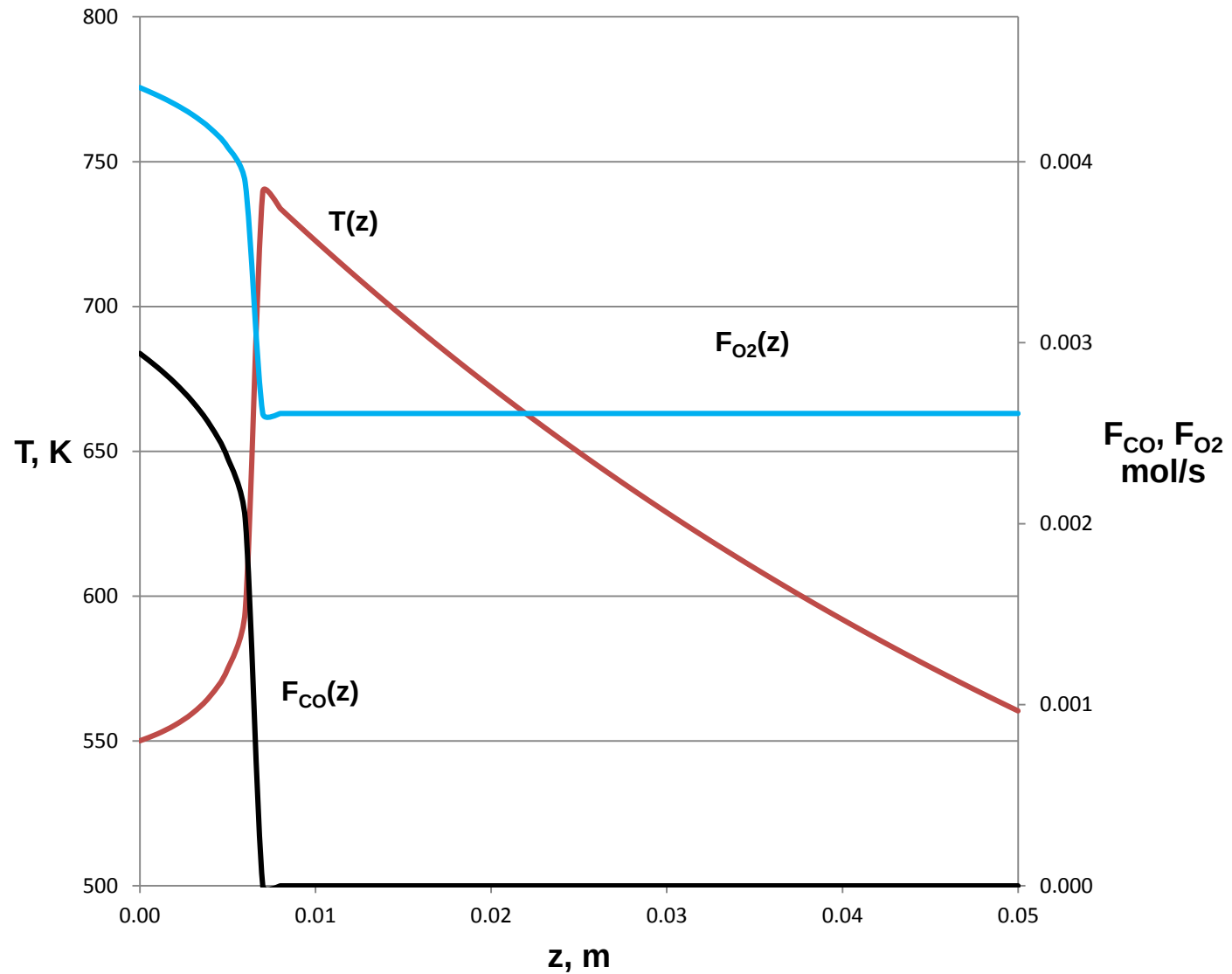
$$\mu_f = 3.44 \times 10^{-5} \text{ Pa.s}$$

Data supplement:

$$\omega = 230 \text{ W/(m}^2\text{K)} \quad T_m = 325 \text{ K}$$

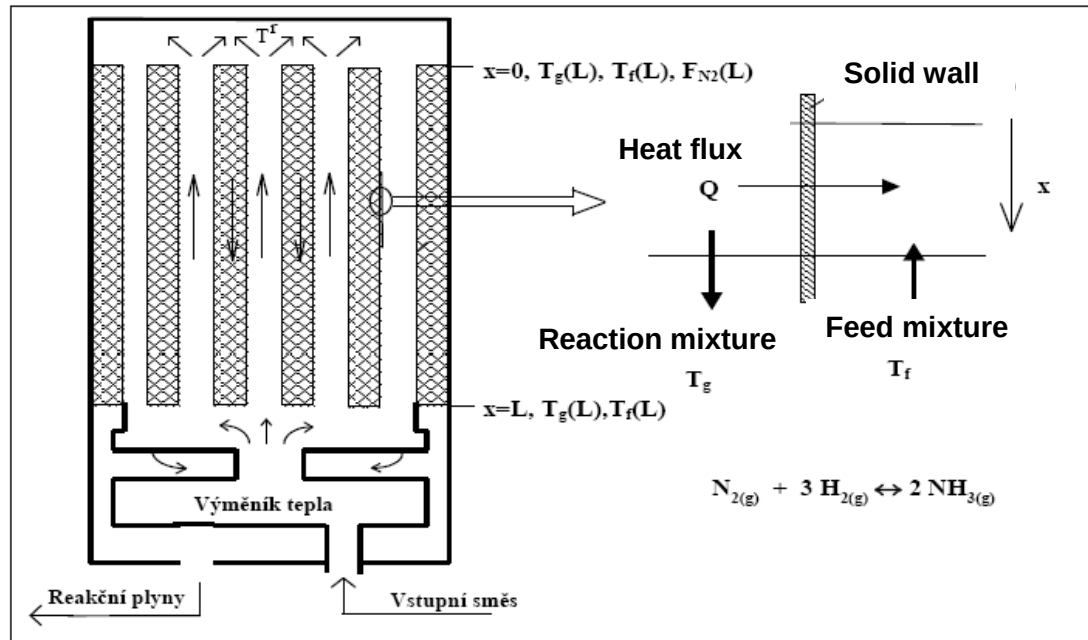
$$T_o = 500 \text{ K} \quad P_o = 202 \text{ kPa}$$

Numerical integration done by SIRK42E



Discussion: internal x external mass and heat transfer

Ammonia synthesis catalytic reactor



$$\frac{dT_f}{dx} = \frac{k_c S_1}{G c_{pf}} (T_f - T_g)$$

$$\frac{dT_g}{dx} = \frac{k_c S_1}{G c_{pg}} (T_f - T_g) + \frac{(-\Delta H_r)}{G c_{pg}} R_{N_2}$$

$$\frac{dF_{N_2}}{dx} = -R_{N_2}$$

$$R_{N_2} = K_1(T) \frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - K_2(T) \frac{p_{NH_3}}{p_{H_2}^{1.5}}$$

$$K_1(T) = 1.79 \cdot 10^4 \exp\left[-\frac{87090}{RT}\right] \quad K_2(T) = 2.57 \cdot 10^{16} \exp\left[-\frac{198464}{RT}\right] \quad R = 8,314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Boundary conditions

$x = 0, T_g = T_f, F_{N_2} = F_{N_2}^0$

$x = L, T_f = T_f^0$

Feed temperature	15°C
Feed flow rate	26400 kg/hr
Pressure	190 bar
Length of reactor tubes	$L=8.5$ m
Tube internal diameter	$d_t=0.078$ m
Number of tubes	$N_t=41$
Global heat transfer coefficient	$\omega=2093$ kJ/m ² /hr/K= $2096 \times 10^3 / 3600$ W/m ² /K
Temperature of reaction mixture in catalyst inside of tube	$T_R[K]$
Temperature of reaction mixture in the shell	$T_F[K]$
Component partial pressure	p_i [bar]

1-D pseudo homogeneous model with axial dispersion

$$\varepsilon D_{ai} \frac{d^2 c_i}{dz^2} - v_z \frac{dc_i}{dz} + v_i r_V = 0$$

$$\lambda_{am} \frac{d^2 T}{dz^2} - v_z \rho_g c_{pm} \frac{dT}{dz} + (-\Delta H_r) r_V + \frac{4K}{d_t} (T_m - T) = 0$$

Boundary conditions

$$z = 0 \quad -\varepsilon D_{ai} \frac{dc_i}{dz} + c_i \cdot v_z = c_i^o \cdot v_z \quad -\lambda_{am} \frac{dT}{dz} + v_z \rho_g c_{pm} T = v_z \rho_g c_{pm} T_o$$

$$z = L \quad \frac{dc_i}{dz} = 0 \quad \frac{dT}{dz} = 0$$

Dimensionless form

$$x = \frac{z}{L} \quad Y_i = \frac{c_i}{c_i^o} \quad \vartheta = \frac{T}{T_o}$$

Bilanční rovnice přejdou na tvar

$$\frac{1}{Pe_{Mi}} \frac{d^2 Y_i}{dx^2} - \frac{dY_i}{dx} + Da_i R(Y_k, \vartheta) = 0$$

$$\frac{1}{Pe_H} \frac{d^2 \vartheta}{dx^2} - \frac{d\vartheta}{dx} + \beta R(Y_k, \vartheta) = 0$$

$$x = 0 \quad \frac{1}{Pe_{Mi}} \frac{dY_i}{dx} = Y_i - 1 \quad \frac{1}{Pe_H} \frac{d\vartheta}{dx} = \vartheta - 1$$

$$x = 1 \quad \frac{dY_i}{dx} = 0 \quad \frac{d\vartheta}{dx} = 0$$

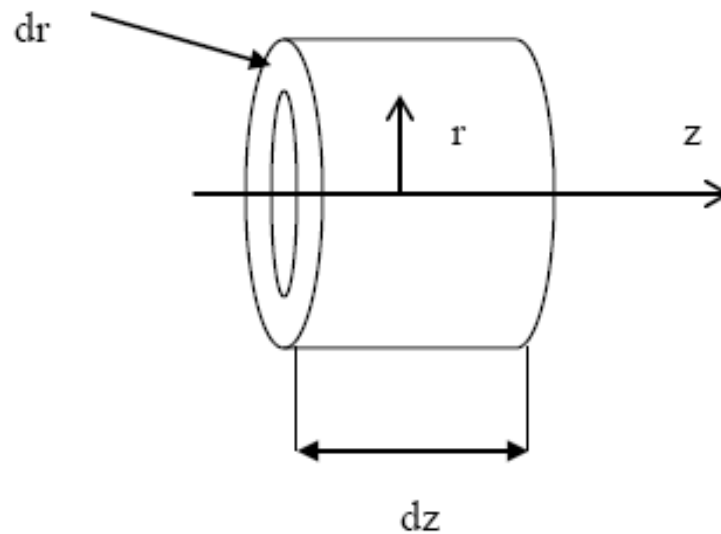
kde

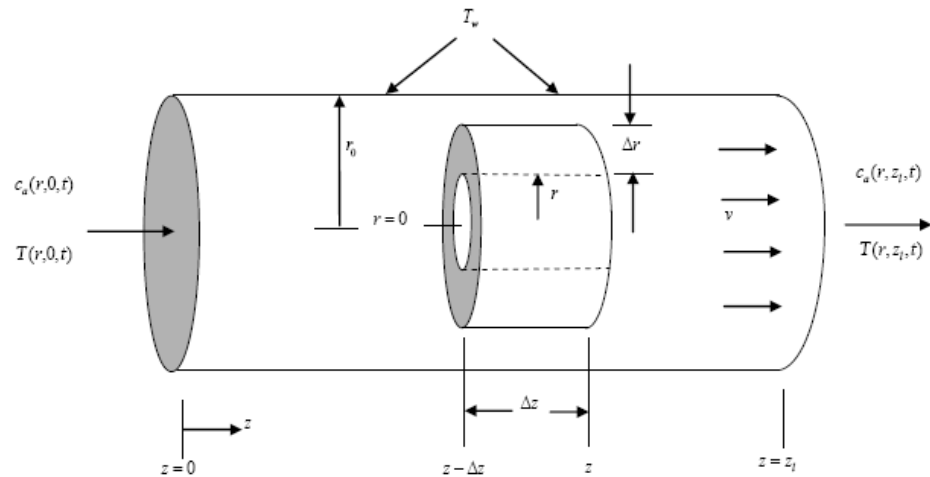
$$Pe_{Mi} = \frac{v_z L}{\varepsilon D_{ai}} \quad Pe_H = \frac{v_z L}{\lambda_{am}} \quad Da_i = \frac{L r_V(c_k^o, T_o)}{c_i^o v_z} \quad \beta = \frac{L r_V(c_k^o, T_o)(-\Delta H_r)}{v_z c_{pm} \rho_g v_z T_o}$$

2-D pseudo homogeneous model with axial and radial dispersion

$$N_i = -D_{ai} \frac{\partial c_i}{\partial z} - D_{ri} \frac{\partial c_i}{\partial r} + y_i \sum_{j=1}^{NS} N_j = -D_{ai} \frac{\partial c_i}{\partial z} - D_{ri} \frac{\partial c_i}{\partial r} + c_i \cdot v$$
$$N_H = -\lambda_{am} \frac{\partial T}{\partial z} - \lambda_{rm} \frac{\partial T}{\partial r} + v \rho_g c_{pm} T$$

Balance element of volume





Balance equations

$$D_{ai} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + D_{ai} \frac{\partial^2 c_i}{\partial z^2} - v_z \frac{\partial c_i}{\partial z} + v_r r_r = 0$$

$$\lambda_{am} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \lambda_{am} \frac{\partial^2 T}{\partial z^2} - v_z \rho_g c_{pm} \frac{\partial T}{\partial z} + (-\Delta H_r) r_r = 0$$

Boundary and initial conditions

$$z = 0, \quad 0 < r < r_0$$

$$-D_{ai} \frac{\partial c_i}{\partial z} + v c_i = v c_i^o$$

$$-\lambda_{am} \frac{\partial T}{\partial z} + v \rho_g c_{pm} T = v \rho_g c_{pm} T_o$$

$$r = r_0$$

$$\frac{\partial c_i}{\partial r} = 0 \quad -\lambda_{am} \frac{\partial T}{\partial r} = h_w (T - T_m)$$

$$r = 0$$

$$\frac{\partial c_i}{\partial r} = 0 \quad \frac{\partial T}{\partial r} = 0$$

Fluidized bed catalytic reactor

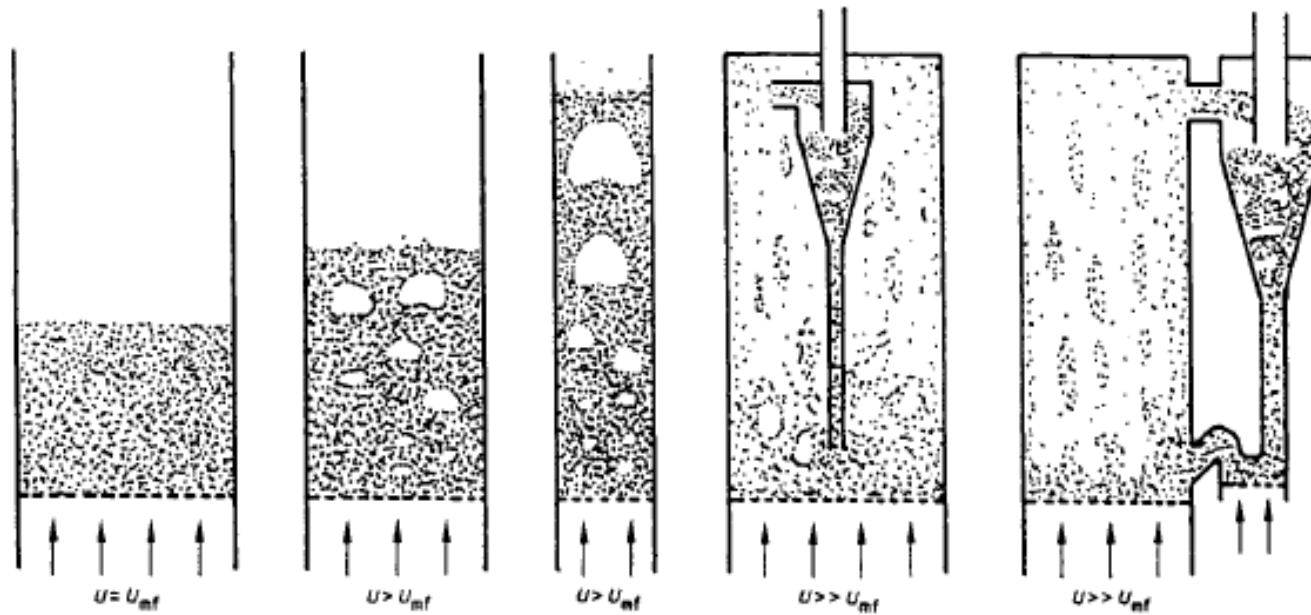


Figure 2. Forms of gas-solids fluidized beds.

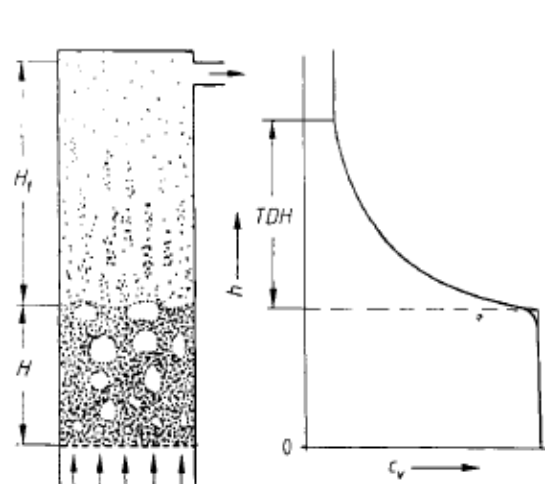


Figure 7. Schematic drawing of fluidized bed and freeboard.

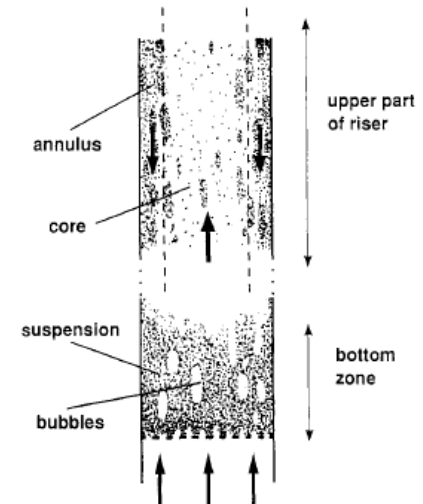


Figure 9. Schematic diagram of flow structure in a circulating fluidized bed.

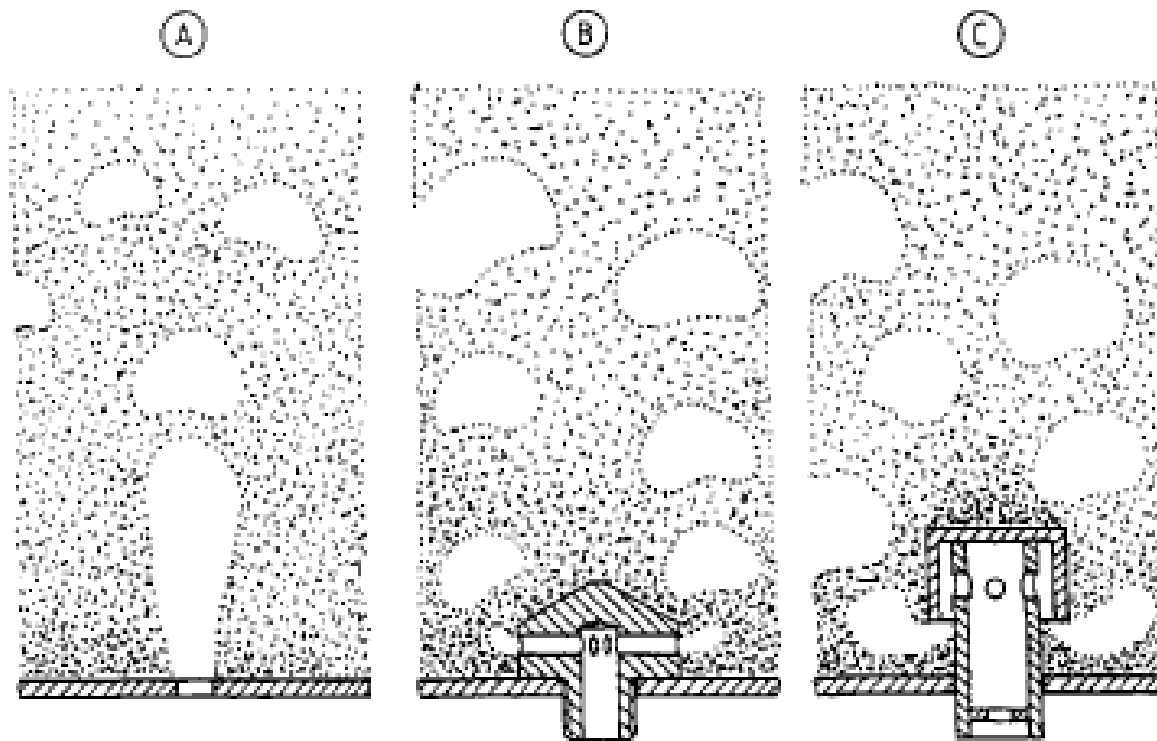


Figure 4. Industrial gas distributors: (A) perforated plate; (B) nozzle plate; (C) bubble-cap plate.

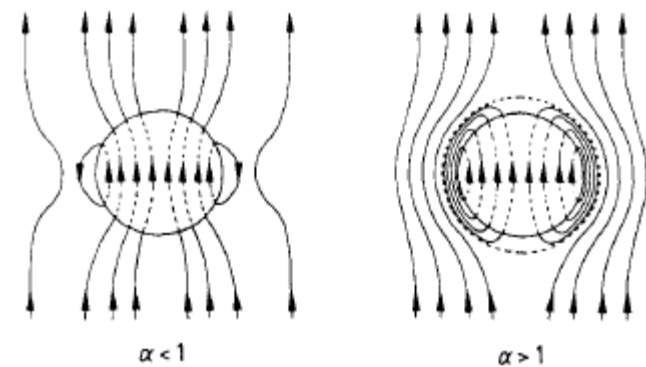


Figure 5. Gas flow for isolated rising bubbles in the D model [30].

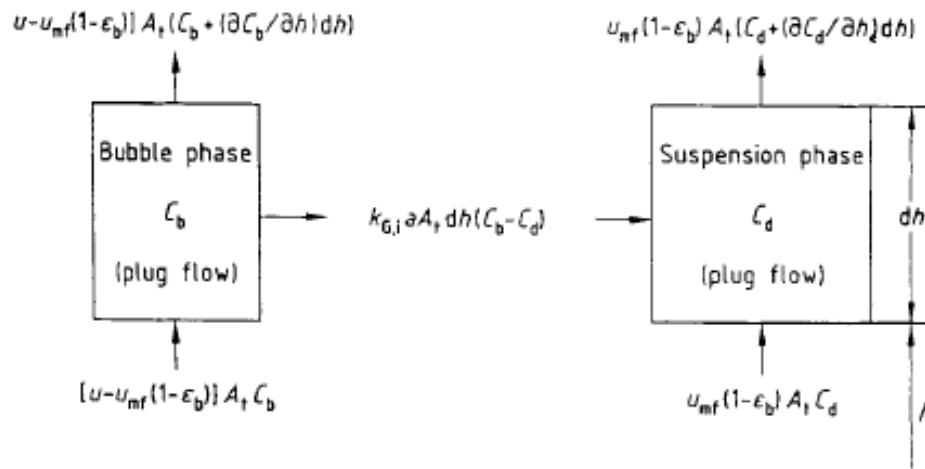


Figure 20. Two-phase model of the fluidized-bed reactor.

$$\varepsilon_b \frac{\partial C_{bi}}{\partial t} = -[u - u_{mf}(1 - \varepsilon_b)] \times \frac{\partial C_{bi}}{\partial h} - k_{G,i} \times a \times (C_{bi} - C_{di}) \quad (26)$$

and, for the suspension phase

$$\begin{aligned} (1 - \varepsilon_b)[\varepsilon_{mf} + (1 - \varepsilon_{mf})\varepsilon_i] \frac{\partial C_{di}}{\partial t} \\ = -u_{mf}(1 - \varepsilon_b) \times \frac{\partial C_{di}}{\partial h} + k_{G,i} \times a \times (C_{bi} - C_{di}) \\ + (1 - \varepsilon_b) \times (1 - \varepsilon_{mf}) \rho_s \sum_{j=1}^M v_{ij} r_j \end{aligned} \quad (27)$$

In eqs 26 and 27 the following simplifying assumptions have been made:

- (i) Plug flow through the suspension phase at an interstitial velocity (u_{mf}/ε_{mf}).
- (ii) Bubble phase in plug flow, bubbles are solids free.
- (iii) Reaction in suspension phase only.
- (iv) Constant-volume reaction (Ref. 99 shows how to handle a change in the number of moles).
- (v) Sorption effects are neglected (see Ref. 102 for handling sorption).

Here ε_i is the porosity of the catalyst particles, a is the local mass-transfer area per unit of fluidized-bed volume, which can be calculated as

$$a = \frac{6\varepsilon_b}{d_v} \quad (28)$$

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14. Industrial chemical reactors

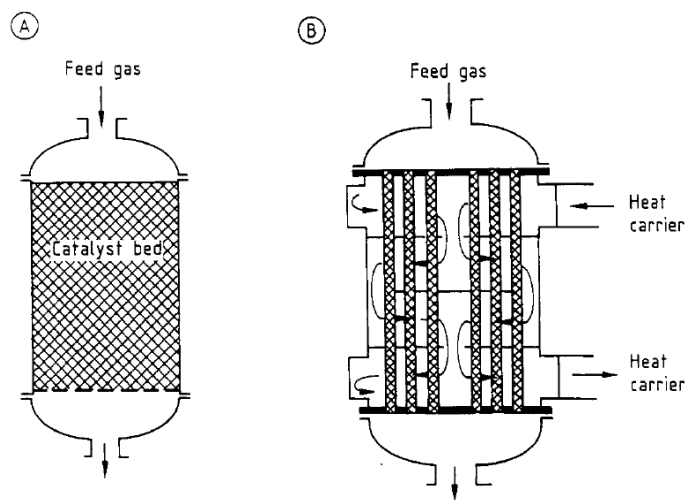


Figure 1. Basic types of catalytic fixed-bed reactors. A) Adiabatic fixed-bed reactor; B) Multitubular fixed-bed reactor.

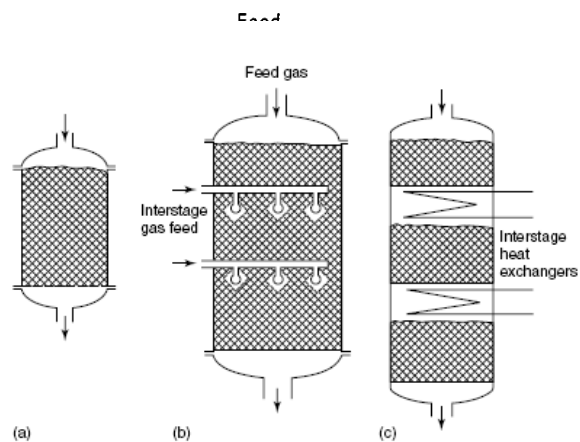


Fig. 12 Development of fixed-bed reactors. (a) Single-bed adiabatic packed-bed reactor; (b) adiabatic reactor with interstage gas feed (ICI concept); (c) multi-bed adiabatic fixed-bed reactor with interstage heat exchange.

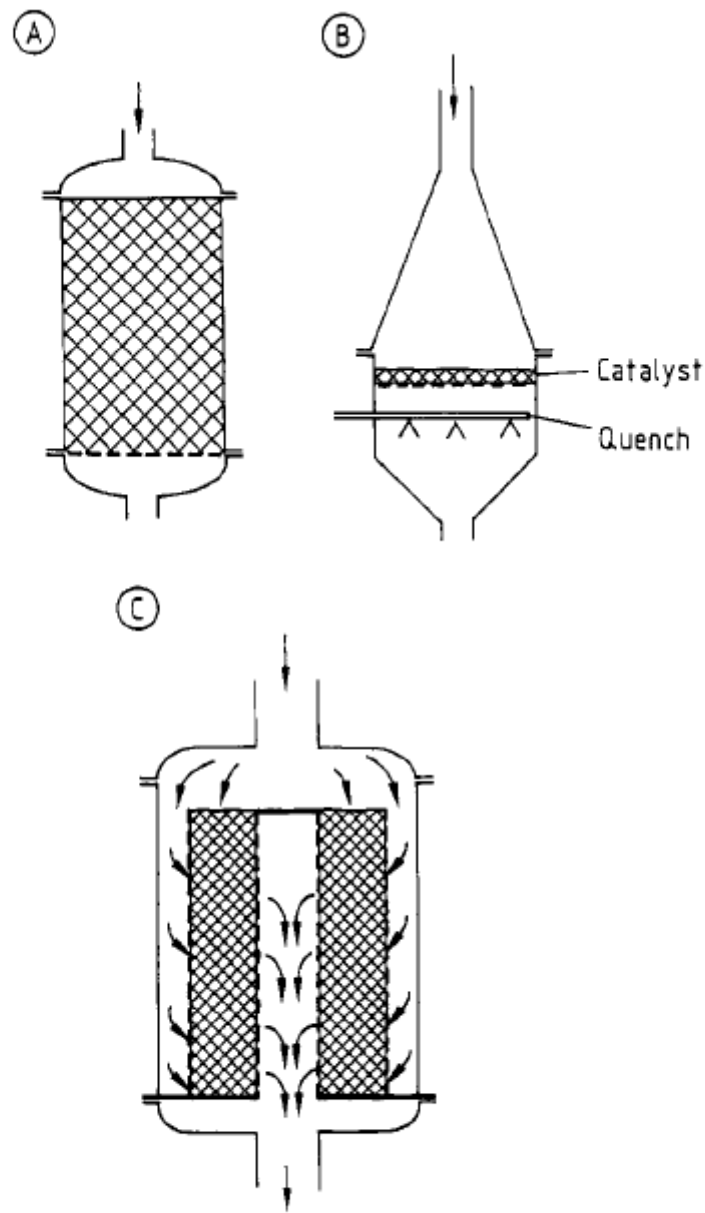


Figure 9. Main design concepts for adiabatic reactors. A) Adiabatic packed-bed reactor; B) Disk reactor; C) Radial-flow reactor.

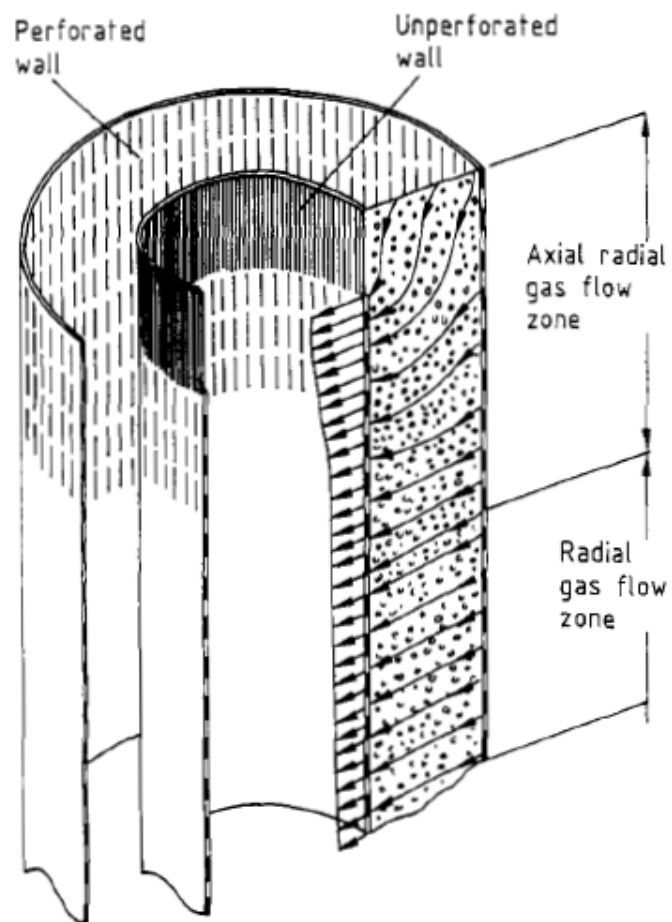


Figure 10. Upper bed closure in a radial-flow reactor [22].

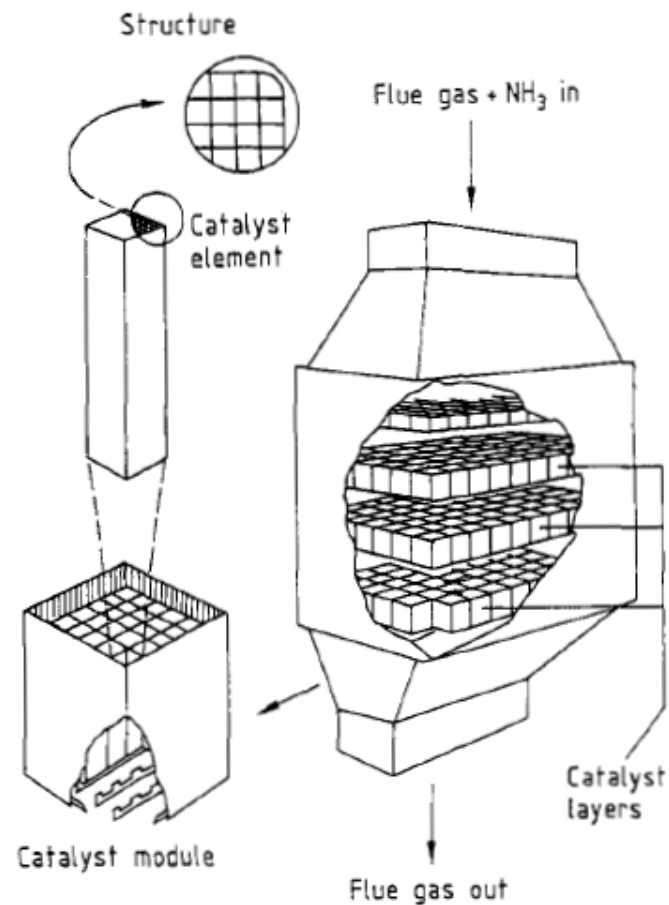


Figure 11. Reaction chamber for removal of nitrogen oxides from power station flue gases [23].

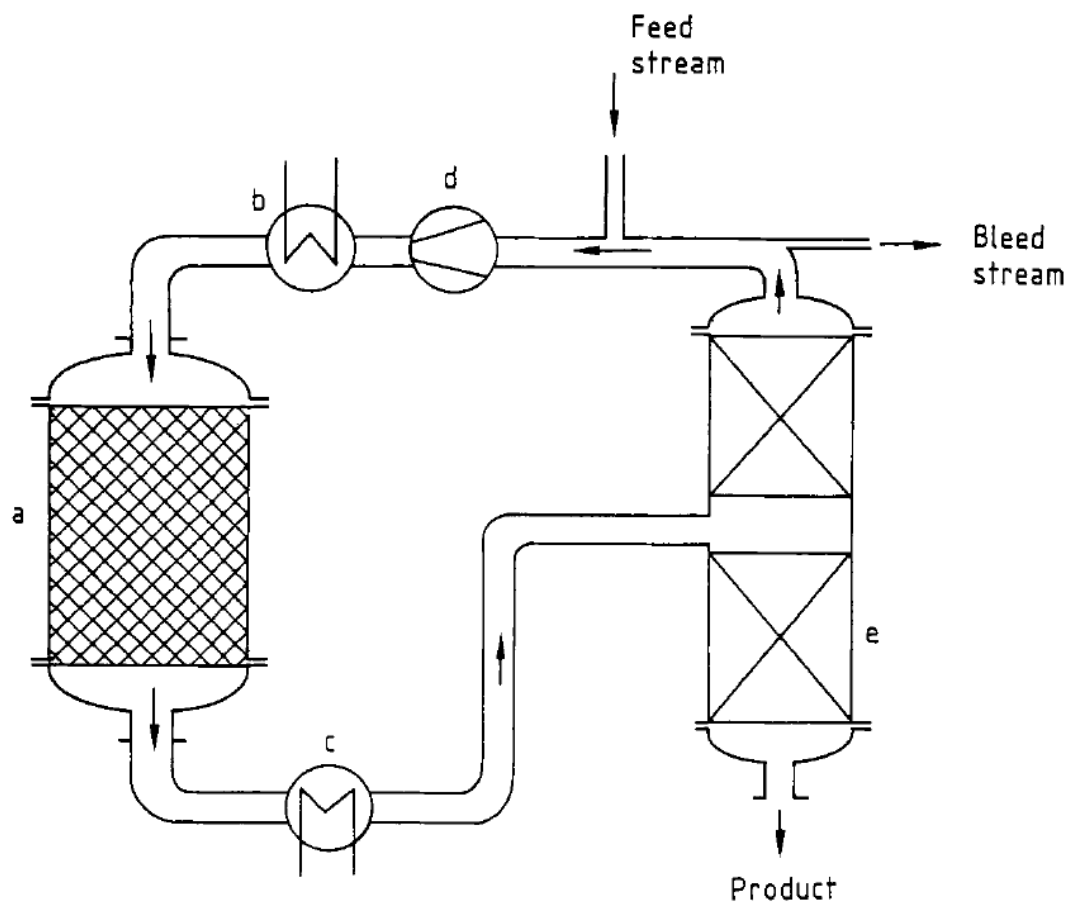


Figure 2. Reaction cycle for synthesis reactions with incomplete conversion. a) Fixed-bed reactor; b) Feed Preheater; c) Exit cooler; d) Recirculation compressor; e) Separation device.

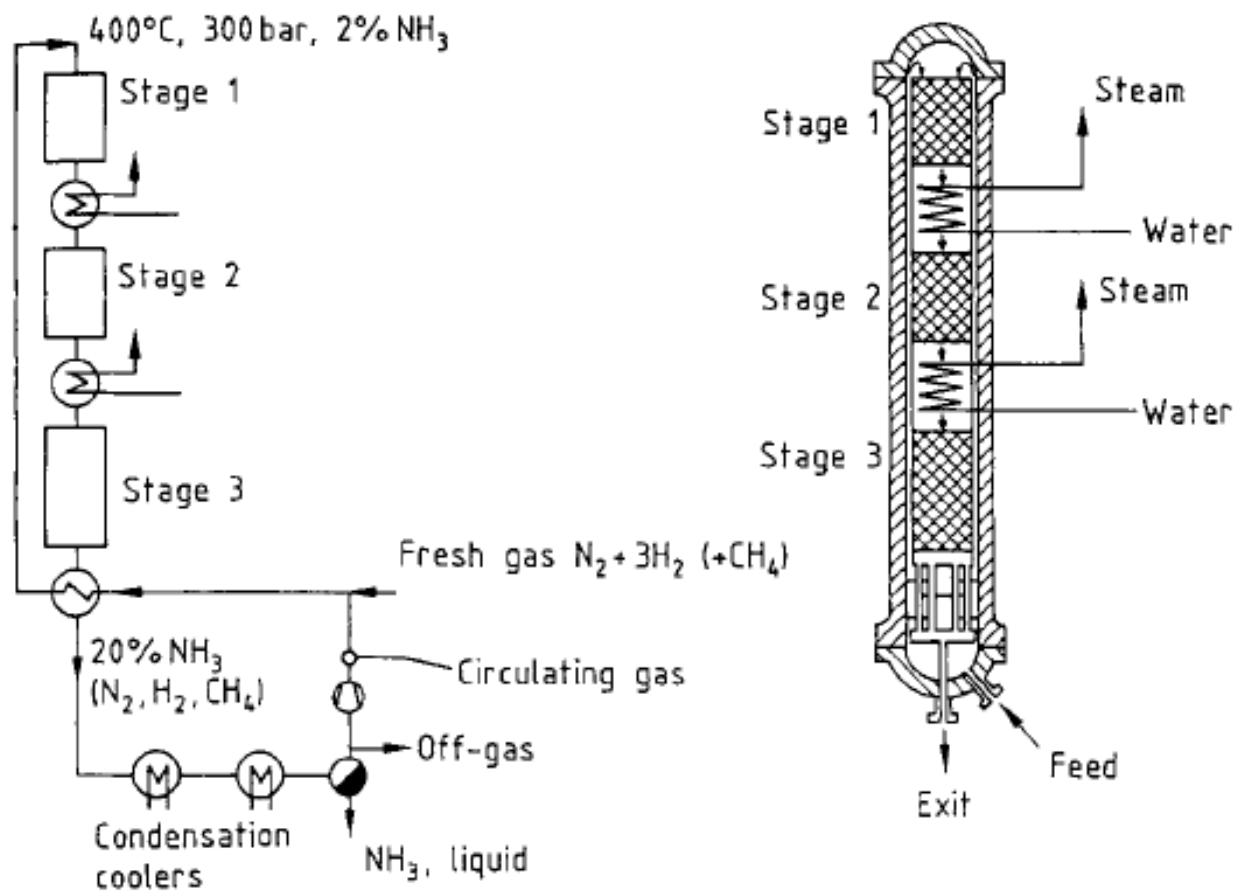


Figure 15. Schematic of a multistage reactor for ammonia synthesis.

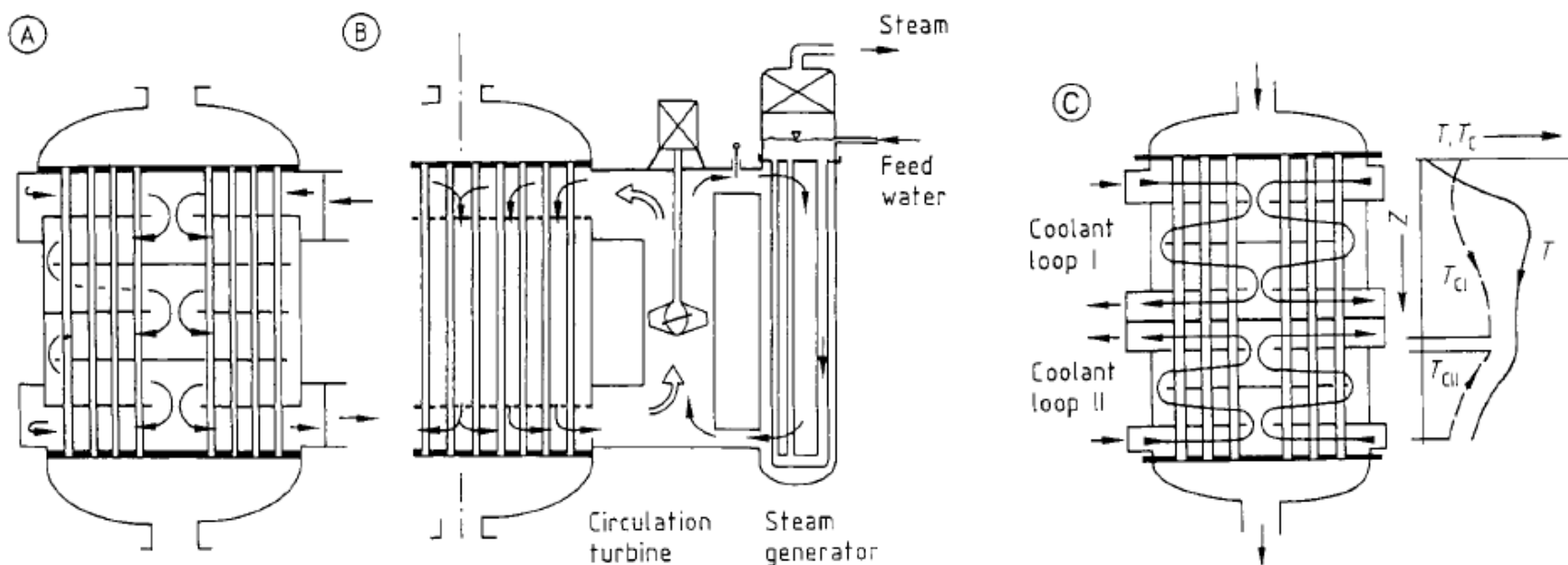


Figure 16. Heat transfer medium control in tube-bundle fixed-bed reactors. A) Cross flow; B) Parallel flow; C) Multiple cooling sections.

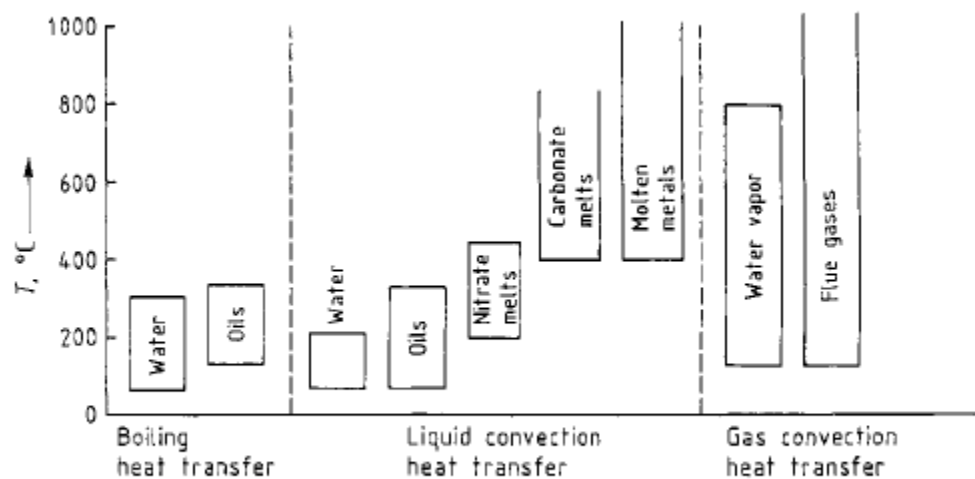
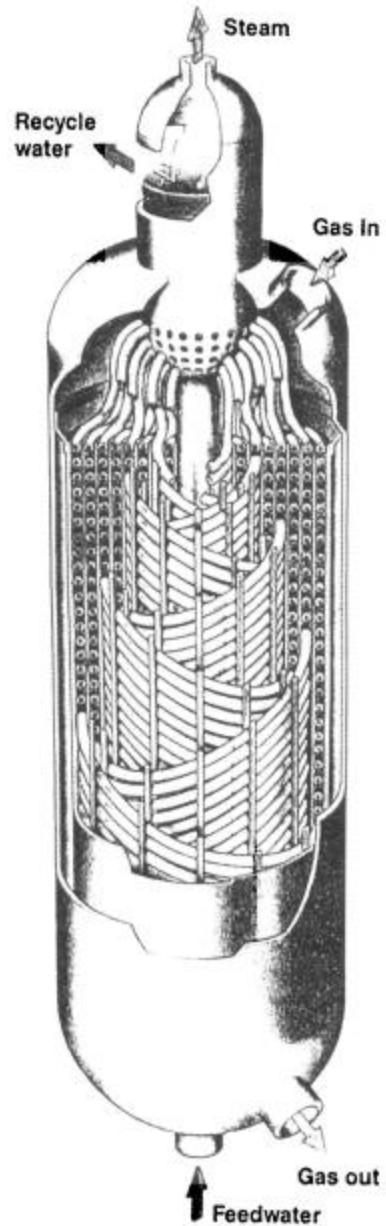


Figure 17. Application ranges for common heat transfer media.

A)



B)

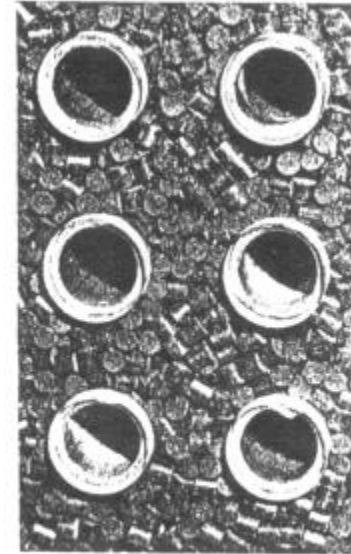


Figure 19. A) Design concept of the Linde isothermal reactor for methanol synthesis; B) Cut through the tube bundle surrounded by catalyst pellets (from [26]).

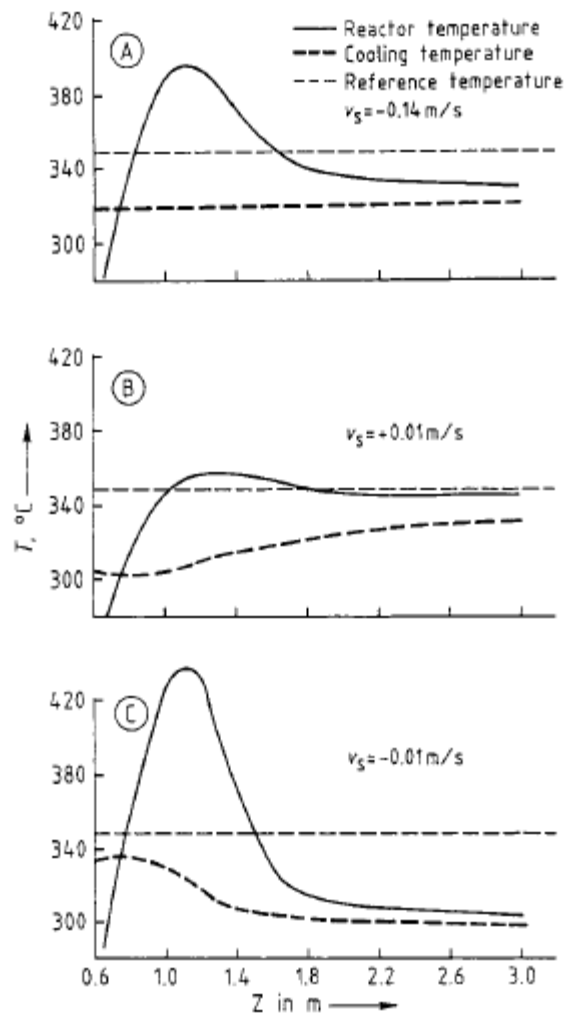


Figure 20. Influence of the coolant flow direction and flow velocity v_s on the reaction temperature profile. A) Isothermal; B) Cocurrent flow; C) Countercurrent flow.

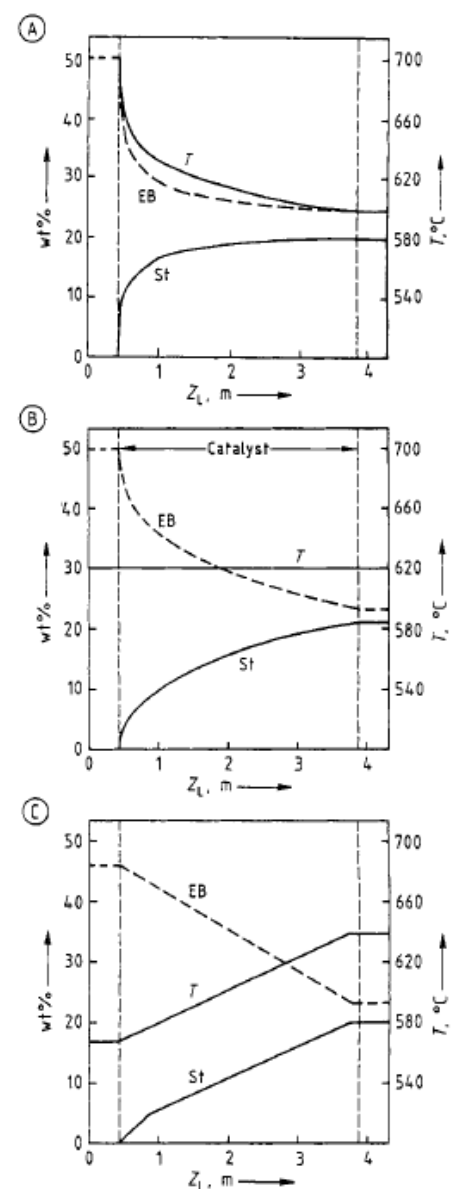


Figure 21. Influence of the heating strategy on the temperature and concentration profiles in styrene synthesis. A) Adiabatic; B) Isothermal; C) Countercurrent heating. EB = ethylbenzene; St = styrene.

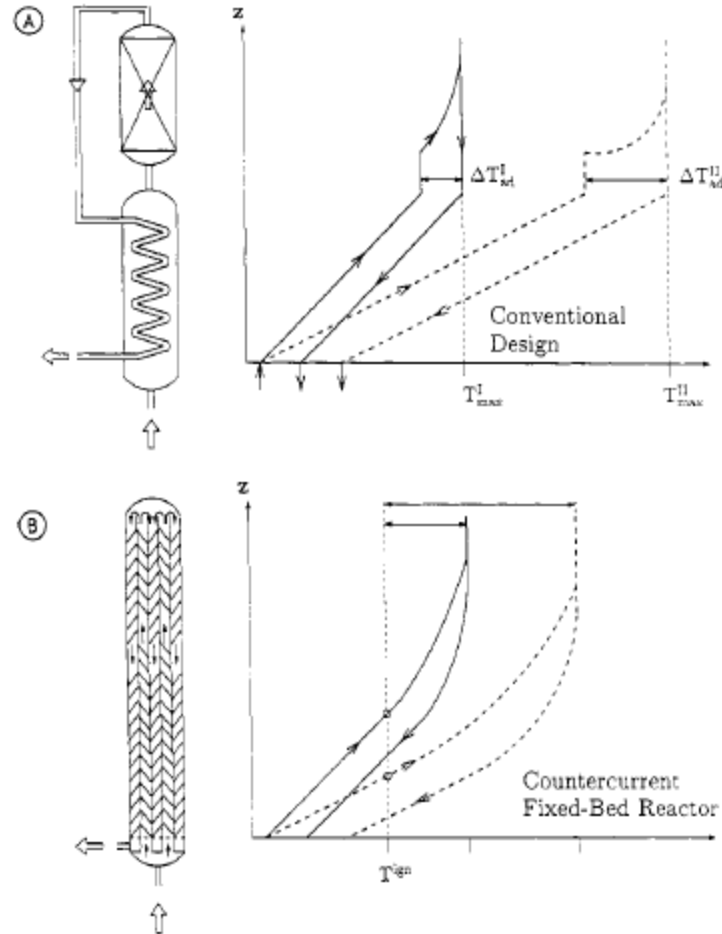


Figure 23. Autothermal fixed-bed reactors with recuperative heat exchange. Basic design and typical temperature profiles. A) Conventional design with separate heat exchanger; B) Countercurrent fixed-bed reactor.

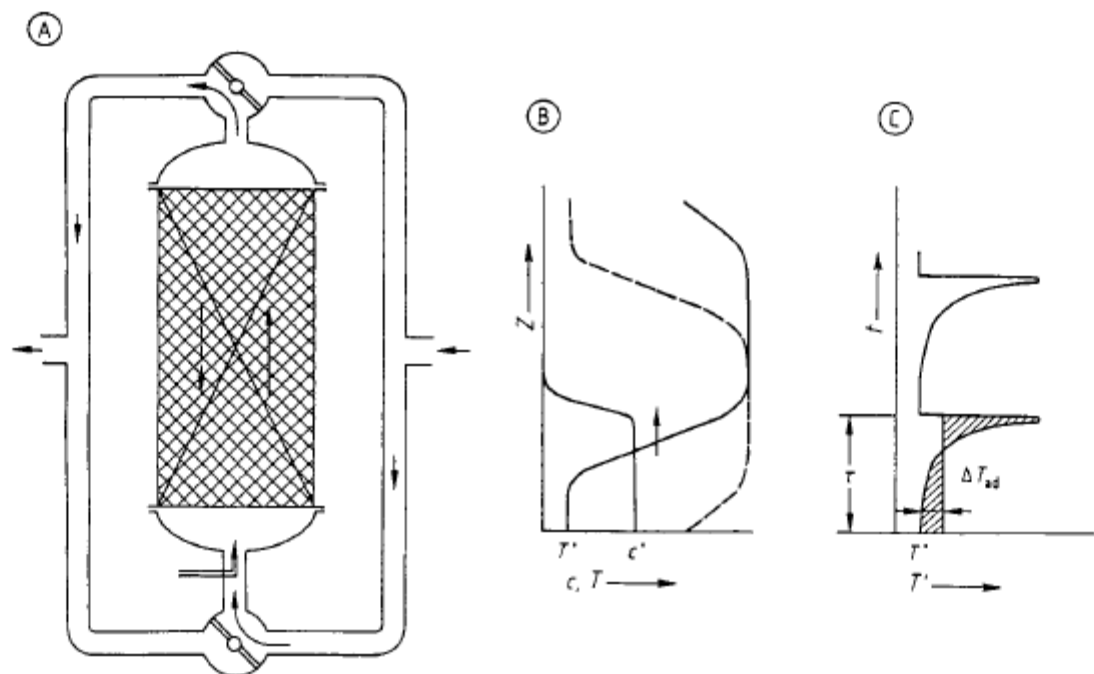


Figure 24. Autothermal reaction control with direct (regenerative) heat exchange for an irreversible reaction [14]. A) Basic arrangement; B) Local concentration and temperature profiles prior to flow reversal in steady state; C) Variation of outlet temperature with time in steady state.

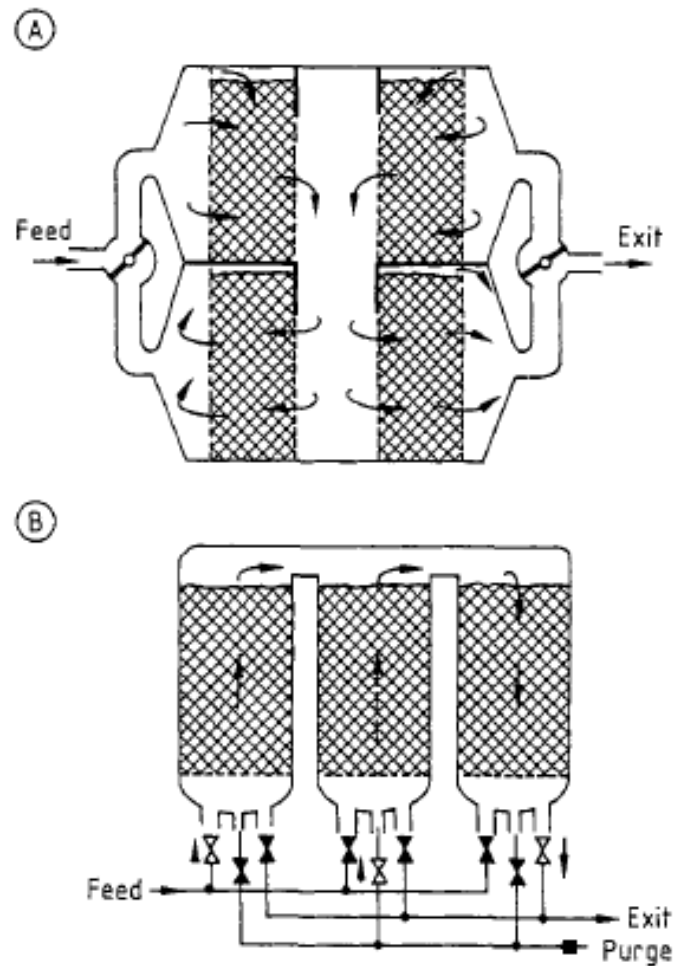
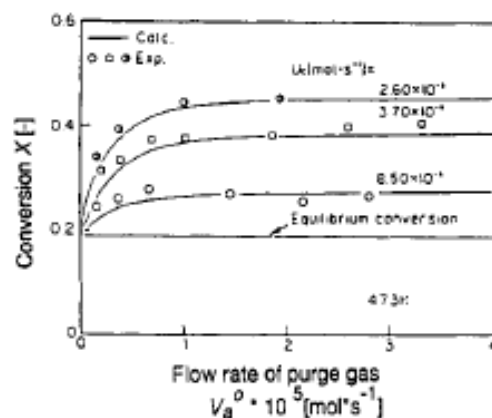
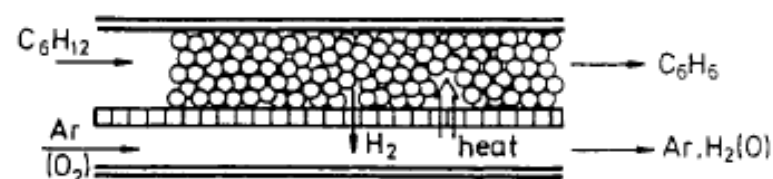
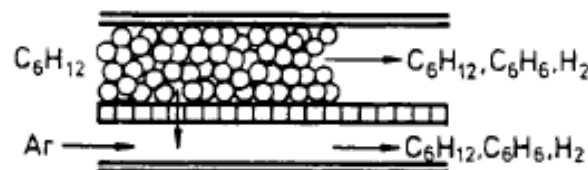
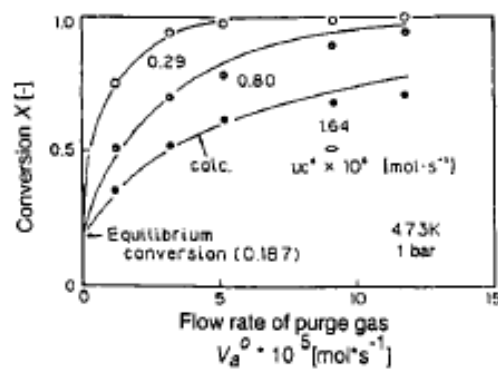


Figure 26. Alternative arrangements for autothermal reactor design with periodic flow reversal. A) Radial-flow concept; B) Multiple-bed arrangement.



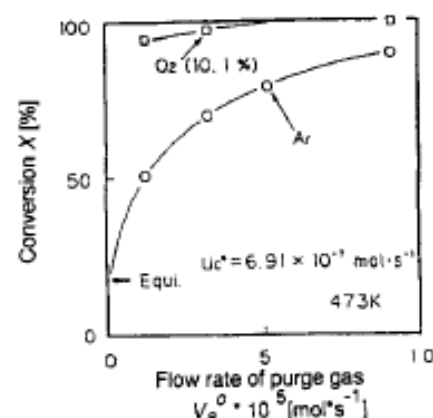
a)

microporous membrane



b)

Palladium membrane
without O_2



c)

with O_2

Figure 28. Cyclohexane dehydrogenation in different membrane reactors, adopted from Itoh [55], a) microporous inert membrane; b) H_2 -selective Pd membrane; c) H_2 -selective Pd membrane with combustion on the permeate side (from [56]).

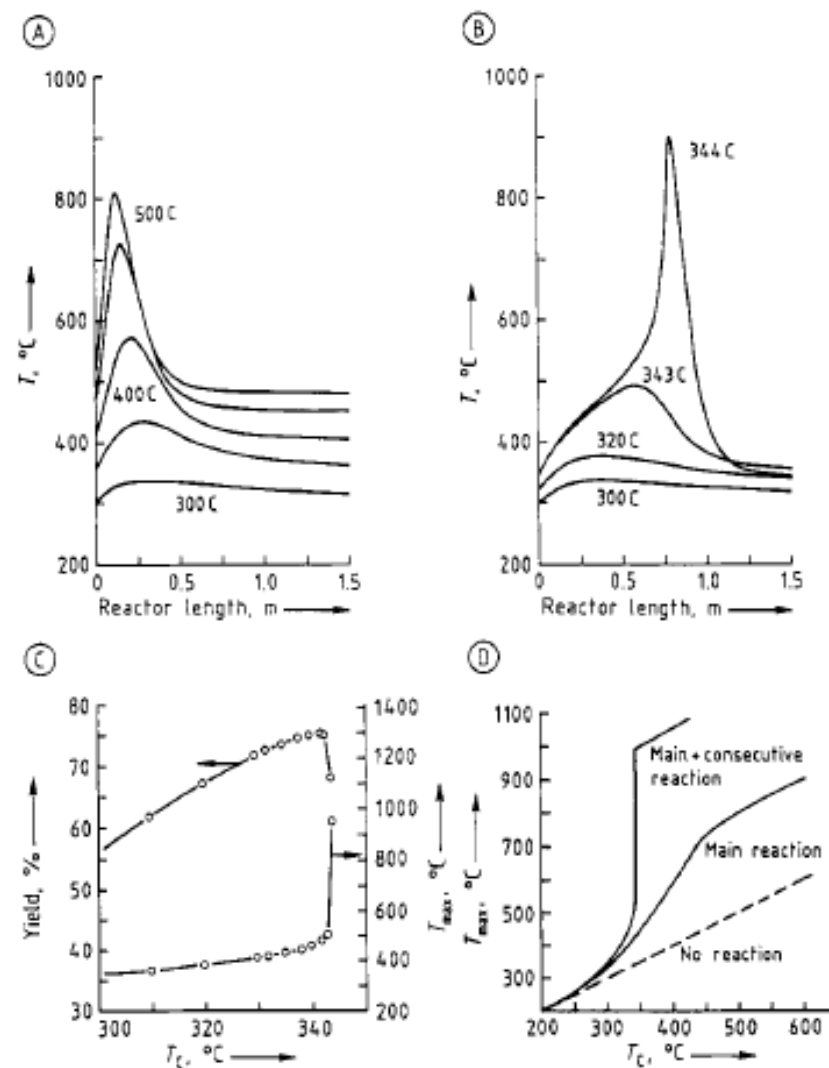


Figure 31. Parametric sensitivity of a partial oxidation reaction in a fixed-bed reactor of typical dimensions as a function of the coolant temperature T_c with $T(z=0) = T_c$. A) Temperature profile over reaction length (main reaction only); B) Temperature profile including total oxidation as side reaction; C) Maximum temperature $T_{\max}$ and yields as a function of coolant temperature T_c in case B; D) $T_{\max}$ as a function of T_c for both cases.

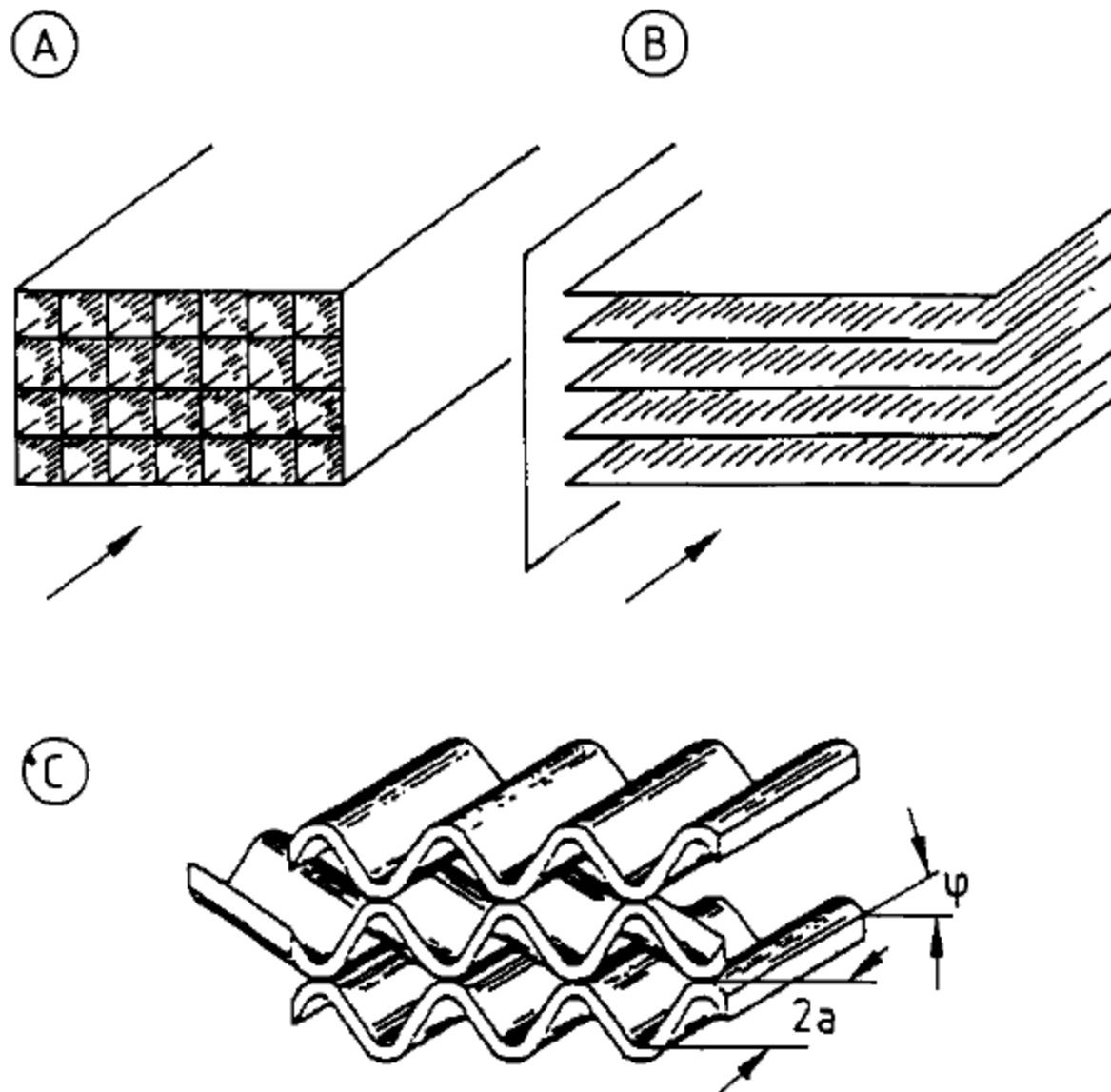


Figure 3. Usual shapes of monolith catalysts. A) Square-channel monolith; B) Parallel-plate monolith; C) Corrugated-plate packing.

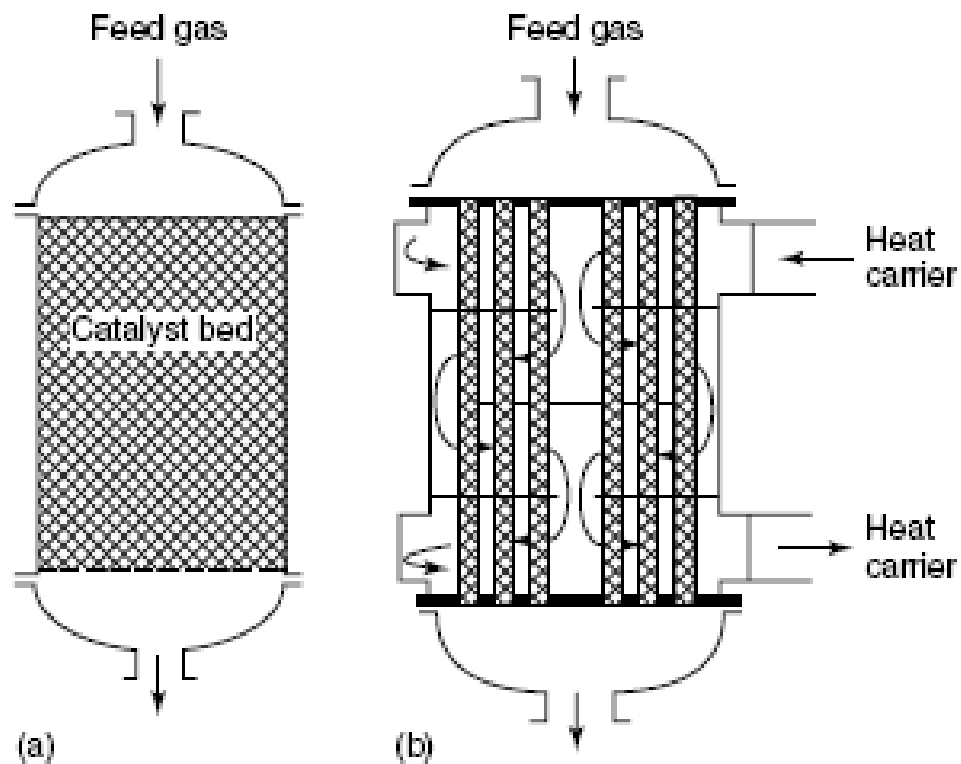


Fig. 1 Basic types of catalytic fixed-bed reactors. (a) Adiabatic fixed-bed reactor; (b) multitubular fixed-bed reactor.

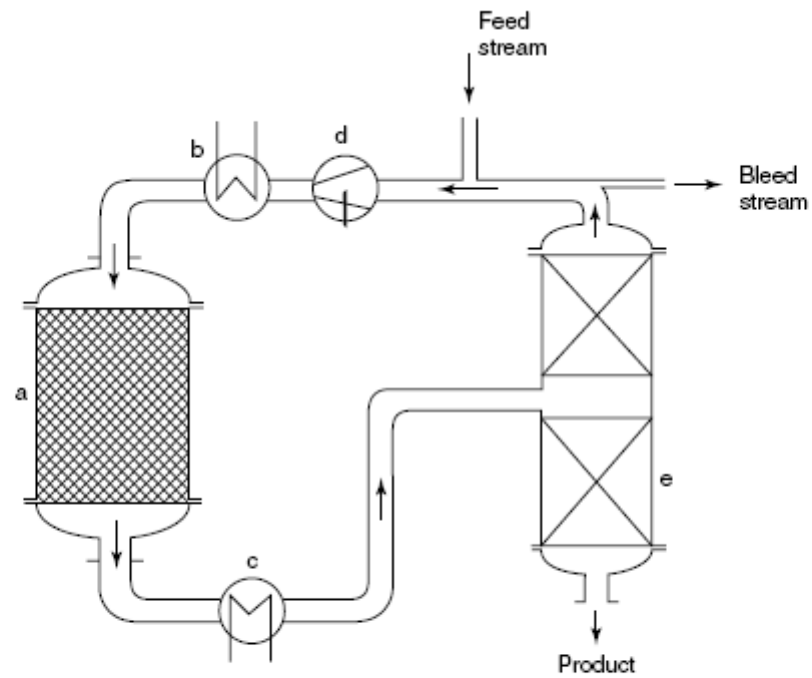


Fig. 2 Reaction cycle for synthesis reactions with incomplete conversion. (a) Fixed-bed reactor; (b) feed preheater; (c) exit cooler; (d) recirculation compressor; (e) separation device.

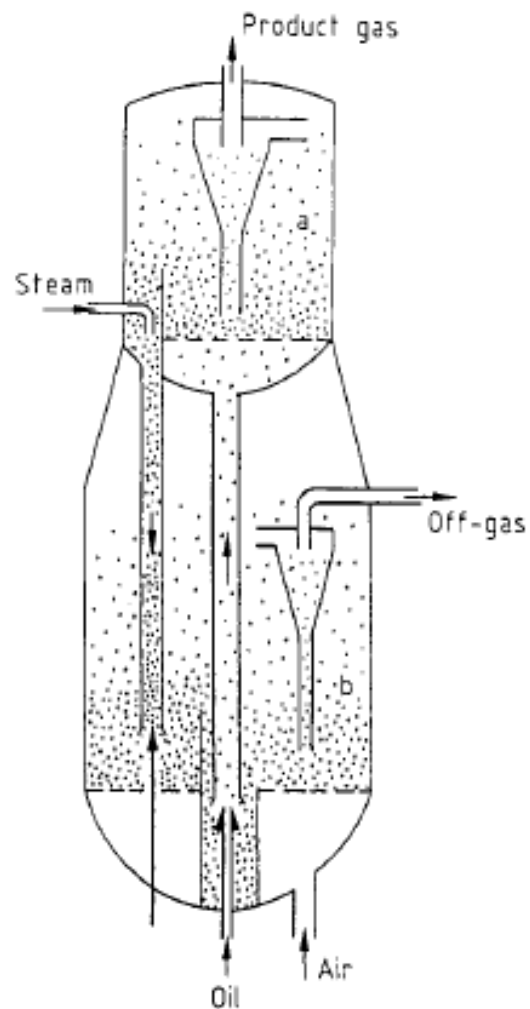


Figure 15. Fluid catalytic cracking process (Kellogg-Orthoflow system; according to Refs 74 and 75: (a) reactor; (b) regenerator.

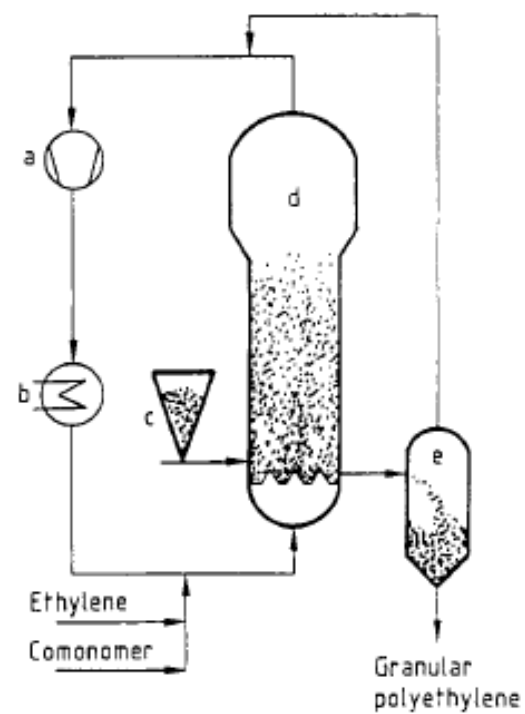


Figure 19. Gas-phase polymerization of ethylene (Unipol process) [2]: (a) compressor; (b) cooler; (c) catalyst feed hopper; (d) reactor; (e) separator.

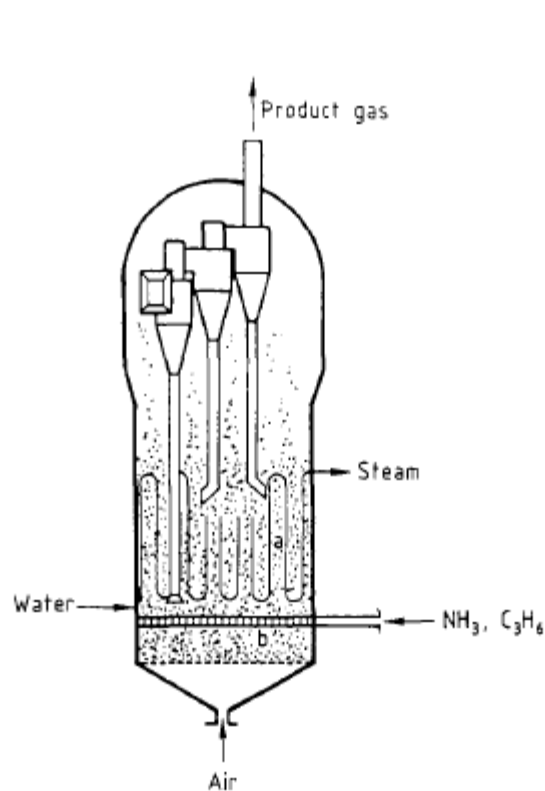


Figure 17. Synthesis of acrylonitrile (Sohio process) [2]: (a) cooler with internals; (b) distributor.

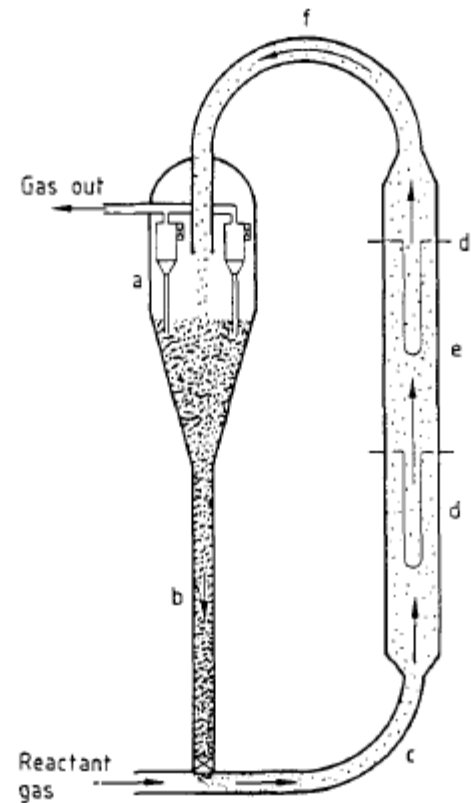


Figure 18. Fischer-Tropsch synthesis in the Synthol reactor [2, 78]: (a) hopper; (b) standpipe; (c) riser; (d) cooler (coil); (e) reactor; (f) gooseneck.

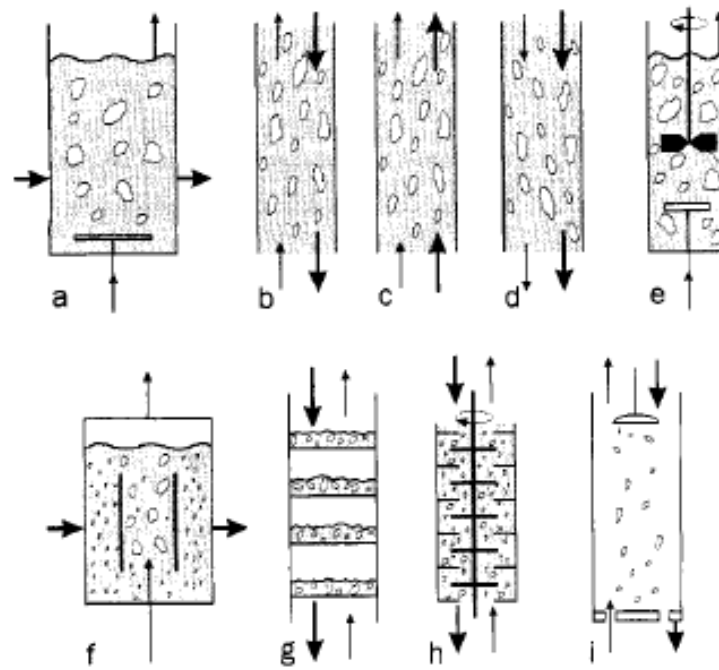
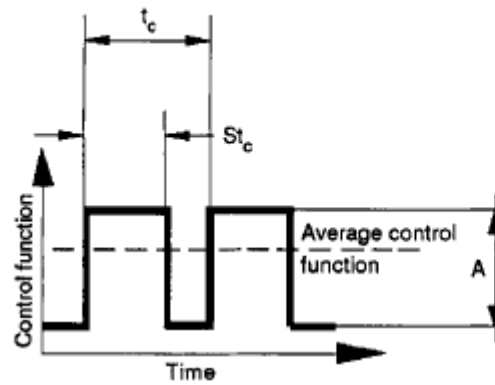
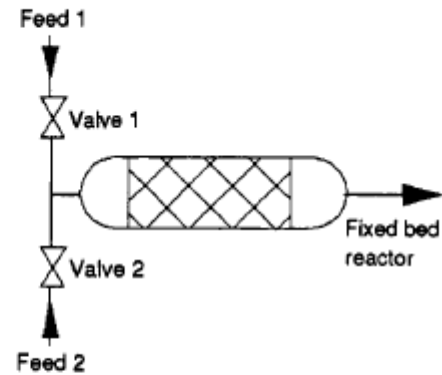


Figure 1. Slurry reactors classified by the contacting pattern and mechanical devices: (a) slurry (bubble) column; (b) countercurrent column; (c) co-current upflow; (d) co-current downflow; (e) stirred vessel; (f) draft tube reactor; (g) tray column; (h) rotating disc or multi-agitated column reactor; (i) three-phase spray column; $\rightarrow$ liquid flow; $\uparrow$ gas flow.



(a)



(b)

Figure 1. (a) Step-wise function of inlet parameters change. (b) Fixed-bed reactor operated at periodic switching between two different feeds that provide for step-wise control.

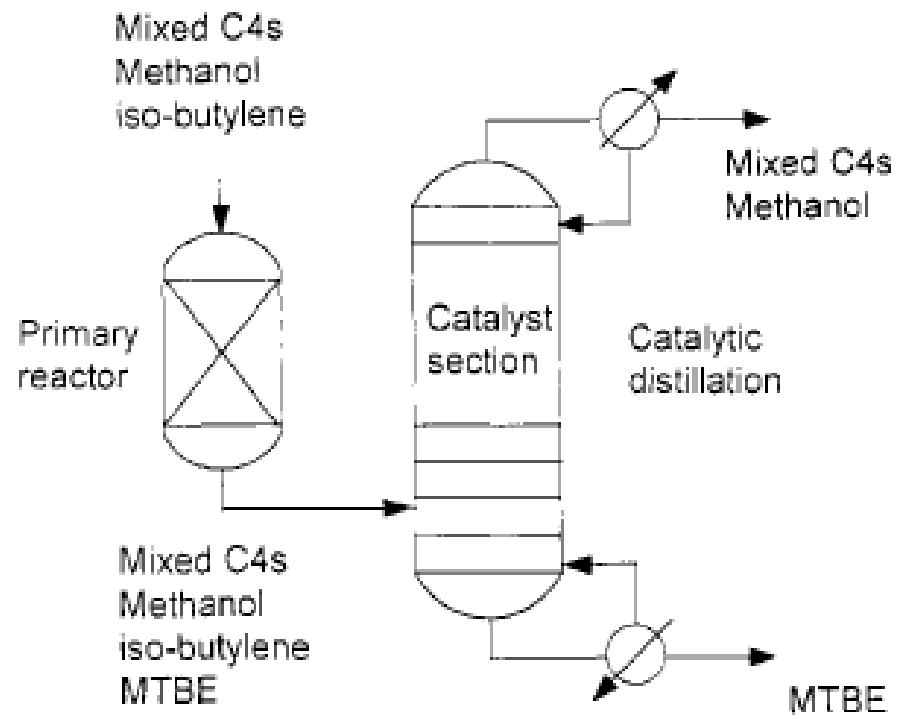


Figure 5. The CR&L catalytic distillation process for MTBE.

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