8. Heterogeneous reaction

- solid – fluid (liquid, gas)

  - Dissolution of solids (e.g. $MgCO_{3(s)} + HNO_{3(l)}$)
  - Chemical Vapor Deposition ($SiH_{4(g)} \rightarrow Si_{(s)} + 2H_2$)
  - Sublimation ($U_{(s)} + 3\ F_{2(g)} \rightarrow UF_{6(g)}$)
  - Reduction of solid oxides ($NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(g)}$)
  - Metals oxidation ($Zn_{(s)} + O_{2(g)} \rightarrow ZnO_{(s)}$)
  - Catalytic reactions

- liquid – gas

  - Dissolution with chemical reaction
    $Cl_{2(s)} + 2NaOH_{(l)} \rightarrow NaOCl_{(l)} + NaCl_{(l)} + H_2O_{(l)}$
    $3NO_{2(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(l)} + NO_{(g)}$

- solid – solid

  - $CoO_{(s)} + Al_2O_{3(s)} \rightarrow CoAl_2O_{4(s)}$

Catalytic heterogeneous reaction

Heat and mass transfer phenomena affect global reaction rate

Catalytic reactions

- **homogeneous catalysis**

$$\begin{array}{l} O_3 + Cl \Rightarrow ClO + O_2 \\ ClO + O_3 \Rightarrow Cl + 2O_2 \\ \hline 2O_3 \Rightarrow 3O_2 \end{array}$$

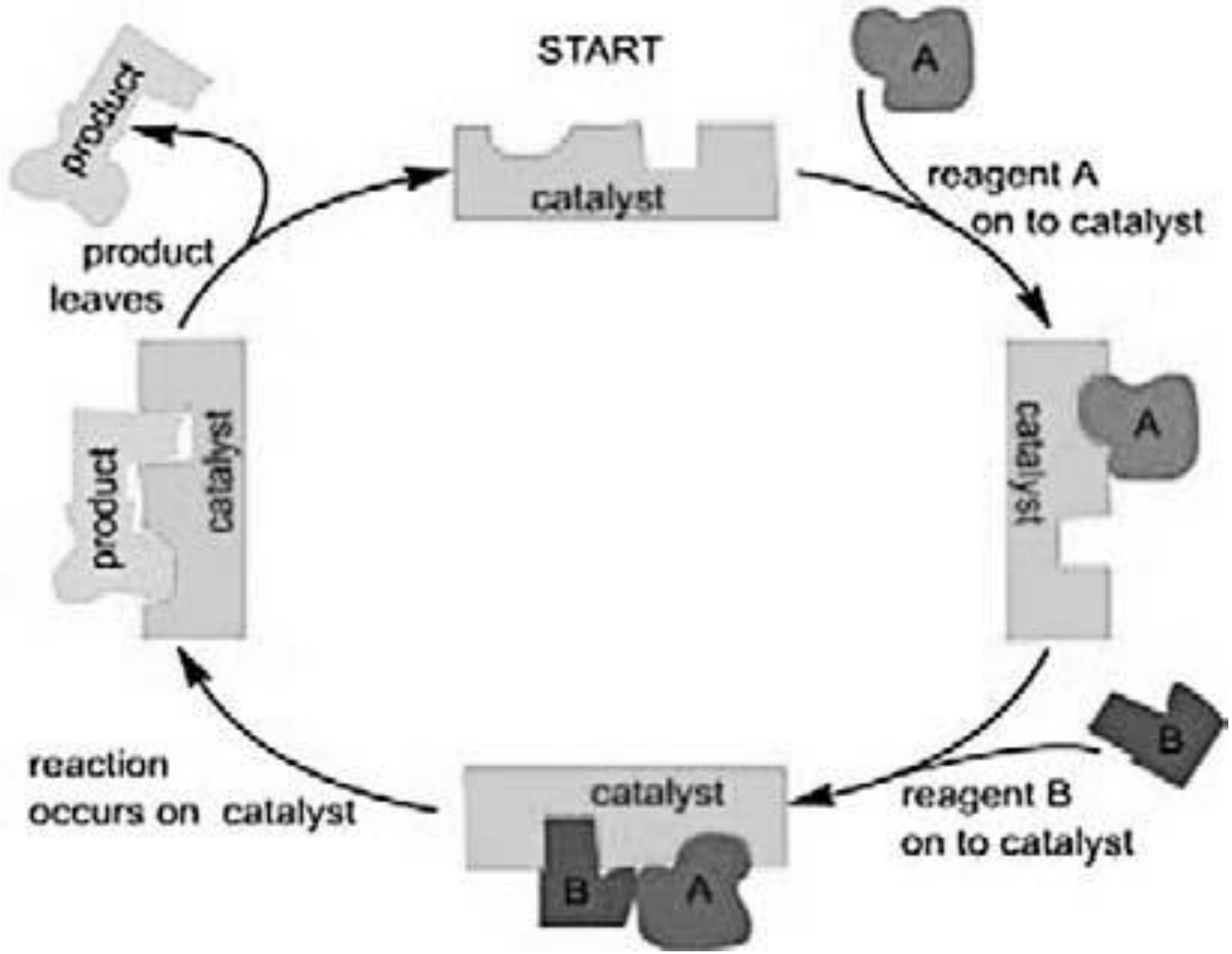
- **Ozone decomposition in the presence of Cl**
- **SO_2 oxidation by NO_x**
- **Esterification catalyzed by acids or bases**
- **Enzymatic catalysis**

- **heterogeneous catalysis**

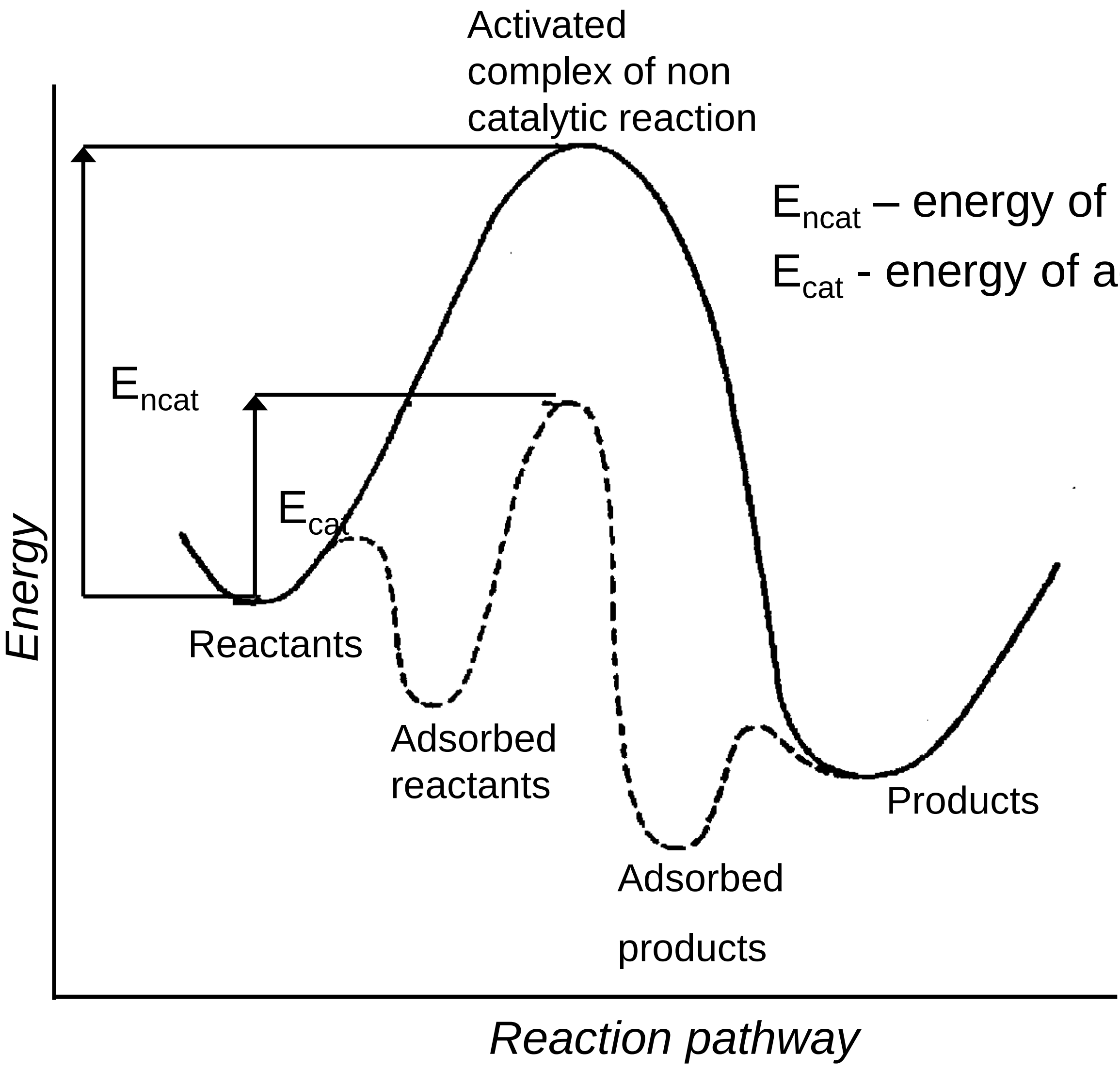
- **NH_3, CH_3OH production**
- **SO_2 to SO_3 oxidation**
- **HDS, HDN processes**
- **Fluid Catalytic Cracking**
- **Hydrogenation**
- **Polymerization (Ziegler-Natta catalysts, metallocens)**

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_2O_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_2H_4, O_2	Ethylene oxide	Ag	$1*10^7$
Unsaturated vegetable oils, H_2	Hydrogenated vegetable oils	Ni	$8*10^6$
C_2H_4	Polyethylene	Cr(II), Ti(III)	$6*10^6$
CH_3OH, O_2	Formaldehyde	Mixed Fe, Mo oxides	$5*10^6$
C_3H_6, NH_3, O_2	Acrylonitrile	Mixed Bi, Mo oxides	$3*10^6$
o -Xylene, O_2	Phthalic anhydride	V_2O_5	$4*10^6$
n-Butane, O_2	Maleic anhydride	V_2O_5	$4*10^5$

Catalytic cycle



Non catalytic x catalytic reaction



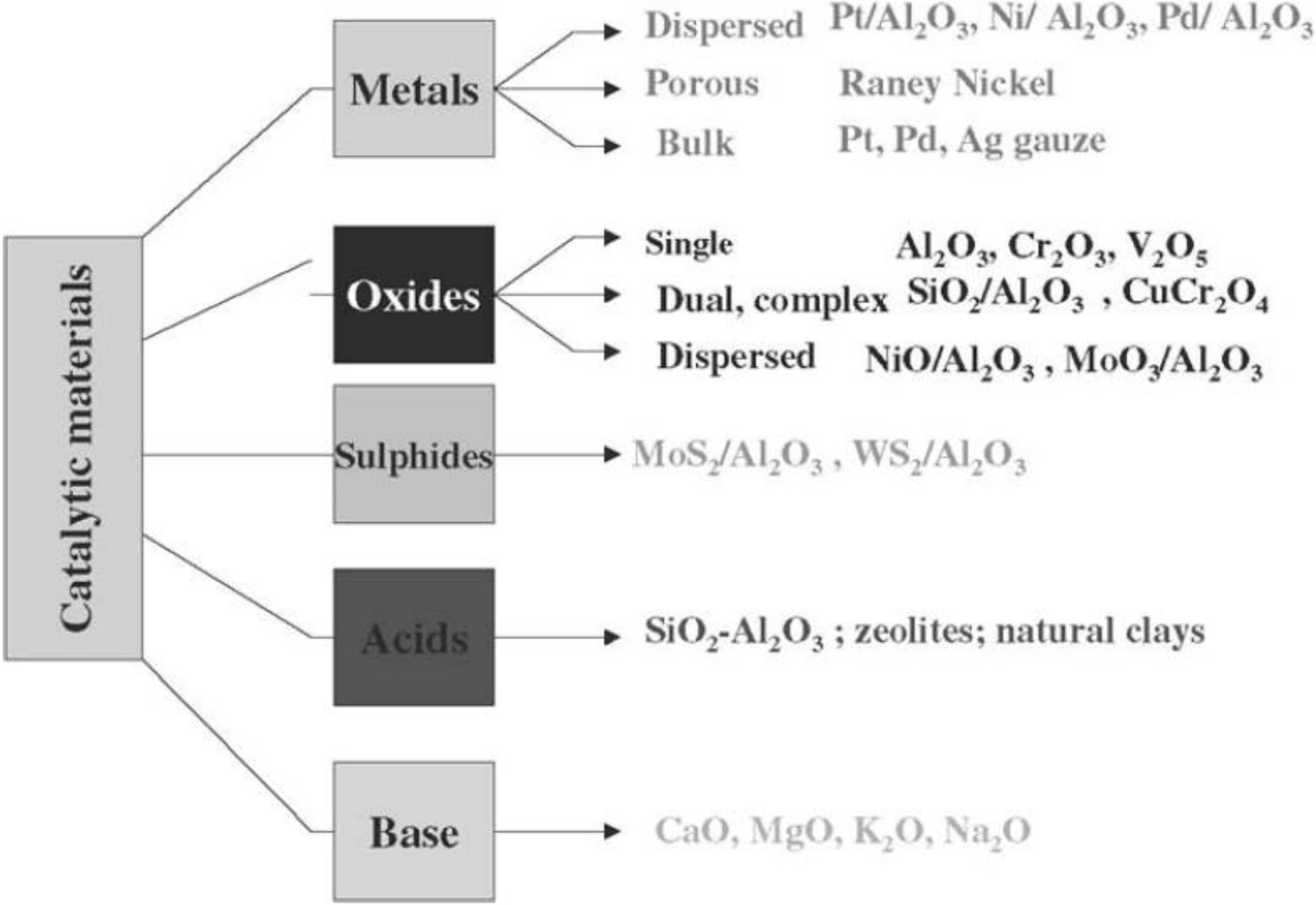
E_{ncat} – energy of activation for non catalytic reaction

E_{cat} - energy of activation for catalytic reaction

$$r_i \sim e^{-\frac{E_i}{RT}}$$

$$\Downarrow$$

The multi-step catalytic reaction can be faster than one-step reaction



Catalytic materials

- **Metals**
  - Dispersed: Pt/Al_2O_3, Ni/Al_2O_3, Pd/Al_2O_3
  - Porous: Raney Nickel
  - Bulk: Pt, Pd, Ag gauze
- **Oxides**
  - Single: Al_2O_3, Cr_2O_3, V_2O_5
  - Dual, complex: SiO_2/Al_2O_3, $CuCr_2O_4$
  - Dispersed: NiO/Al_2O_3, MoO_3/Al_2O_3
- **Sulphides**: MoS_2/Al_2O_3, WS_2/Al_2O_3
- **Acids**: SiO_2-Al_2O_3; zeolites; natural clays
- **Base**: CaO, MgO, K_2O, Na_2O

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.

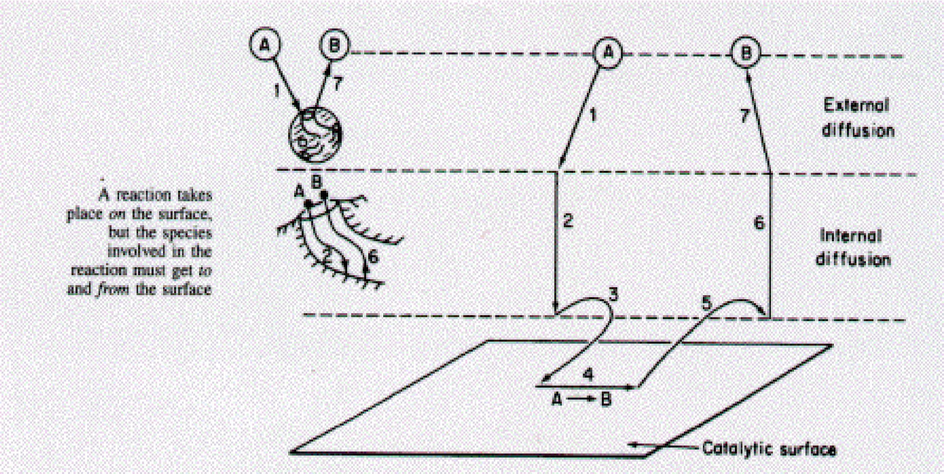
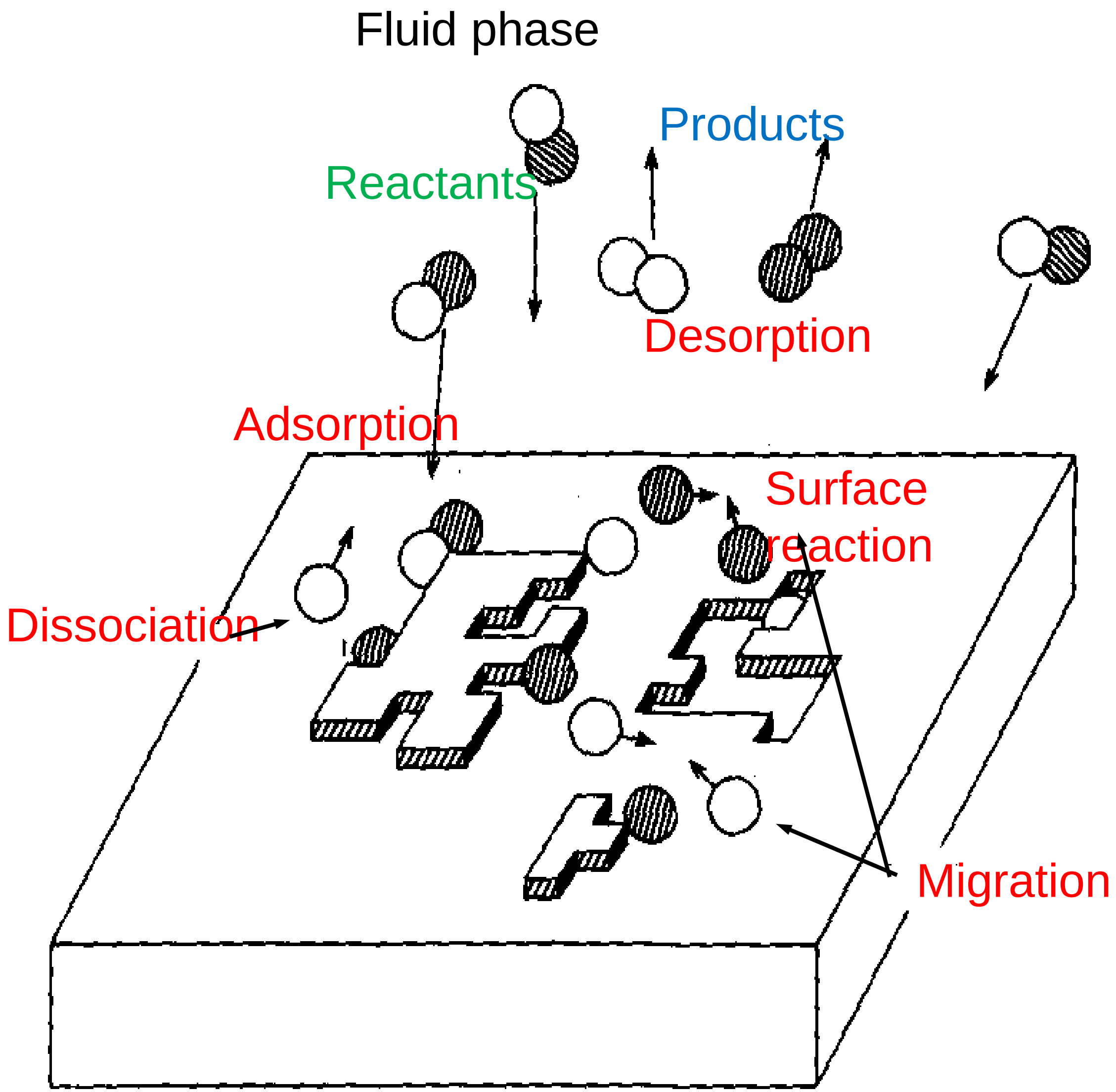


Figure 10-6 Steps in a heterogeneous catalytic reaction.

Elementary steps of catalytic reaction



Reaction rate per mass

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

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

Reaction rate per surface

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

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

Reaction rate per active center (turnover number)

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

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

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

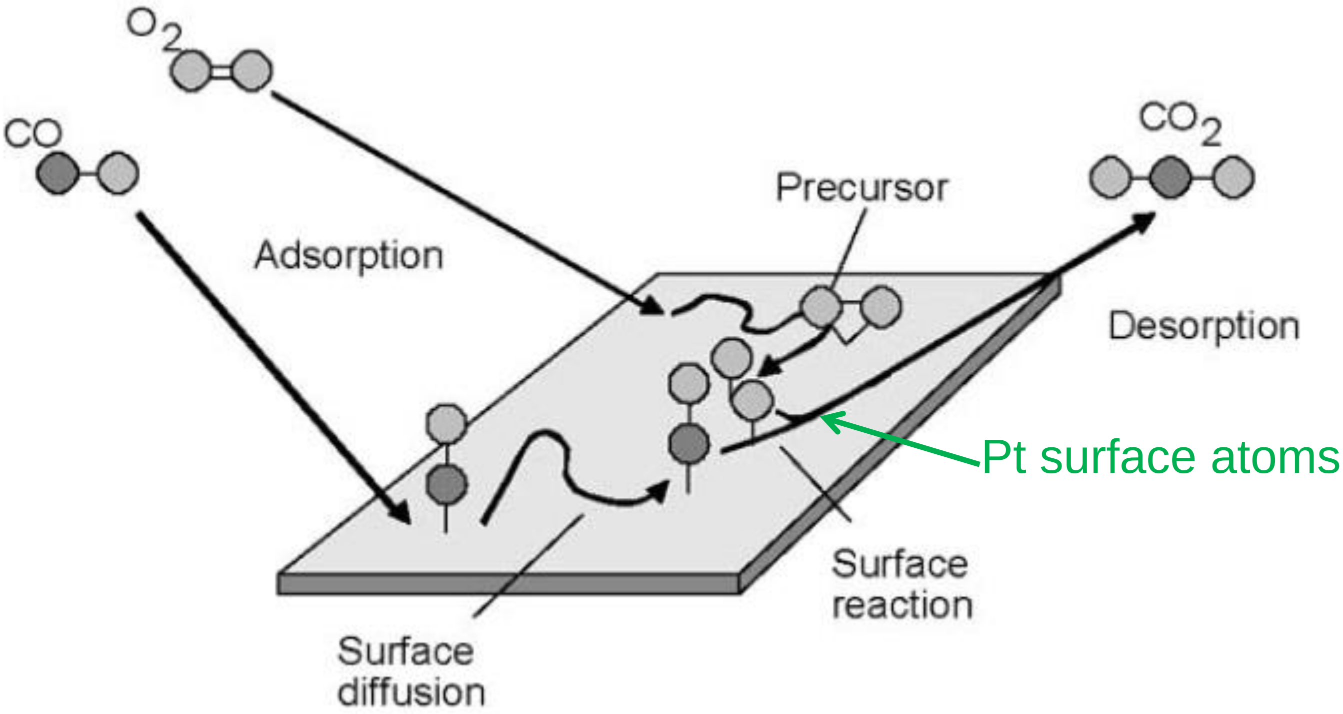
CO oxidation on Pt

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

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

nebo

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$



Elementary steps of catalytic CO oxidation on Pt

1. CO chemisorption

$CO_{(g)} + [*] \leftrightarrow CO^*$	$r_1 = k_{f,1} P_{CO} \Theta_* - k_{b,1} \Theta_{CO}$

2. O_2 dissociative chemisorption

* - Pt surface atoms = Catalytic active centre

$O_{2(g)} + 2[*] \leftrightarrow 2O^*$	$r_2 = k_{f,2} P_{O_2} \Theta_*^2 - k_{b,2} \Theta_O^2$

3. Surface reaction between CO* and O*

$CO^* + O^* \leftrightarrow {}^*CO_2 + *$	$r_3 = k_{f,3} \Theta_{CO} \Theta_O - k_{b,3} \Theta_{CO_2} \Theta_*$

4. CO_2 desorption into gas phase

${}^*CO_2 \leftrightarrow CO_{2(g)} + *$	$r_4 = k_{f,4} \Theta_{CO_2} - k_{b,4} P_{CO_2} \Theta_*$

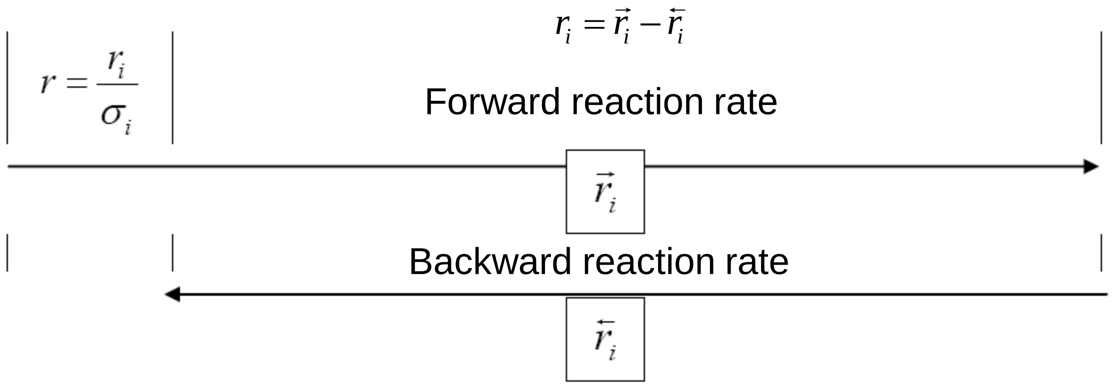
P_i – partial pressures of gaseous components [Pa]

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



$r_i = \vec{r}_i - \overleftarrow{r}_i$

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

Forward reaction rate

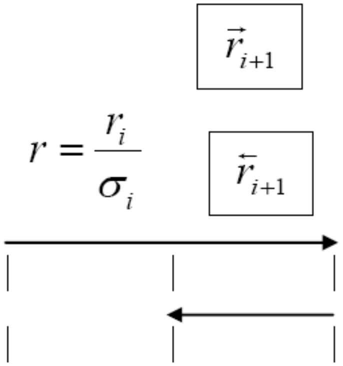
$\vec{r}_i$

Backward reaction rate

$\overleftarrow{r}_i$

Fast step

$\vec{r}_i \cong \overleftarrow{r}_i \Rightarrow$ step is close to the equilibrium



$\vec{r}_{i+1}$

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

$\overleftarrow{r}_{i+1}$

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
$CO_{(g)} + [*] \leftrightarrow CO*$	**2**
$O_{2(g)} + 2[*] \leftrightarrow 2O*$	**1**
$CO* + O* \leftrightarrow *CO_2 + *$	**2**
$*CO_2 \leftrightarrow CO_{2(g)} + *$	**2**
$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$	

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

$$K_{CO} = \frac{k_{f,1}}{k_{b,1}} = \frac{\Theta_{CO}}{P_{CO}\Theta_*} \qquad K_{O2} = \frac{k_{f,2}}{k_{b,2}} = \frac{\Theta_O^2}{P_{O_2}\Theta_*^2} \qquad K_{CO_2} = \frac{k_{b,4}}{k_{f,4}} = \frac{\Theta_{CO_2}}{P_{CO_2}\Theta_*}$$

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

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

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

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

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

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

$C_2H_5OH_{(g)}$ (A_1) → $CH_3CHO_{(g)}$ (A_2) + $H_{(g)}$ (A_3)

catalysts: CuO, CoO a Cr_2O_3
(Franckaerts J., Froment G.F., Kinetic study of the dehydrogenation of ethanol, Chem. Eng. Sci. 19 (1964) 807-818).
Kinetics

$$r_M = \frac{kK_1\left(P_1 - P_2P_3 / K_{eq}\right)}{\left(1 + K_1P_1 + K_2P_2\right)^2}$$

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

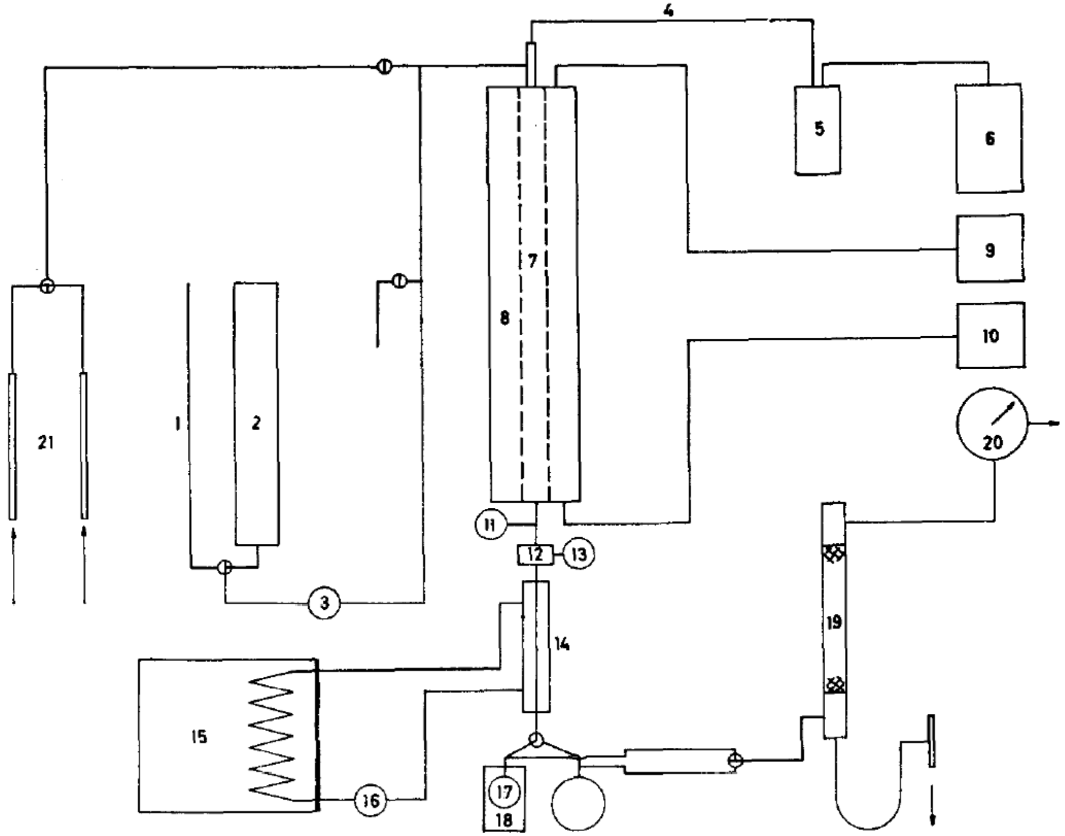


FIG. 1. Apparatus: 1,2, feed burettes; 3, metering pump; 4, thermocouples; 5, ice-bath; 6, mV-recorder; 7, reactor; 8, reactor-mantle; 9,10, variable transformers; 11,13, manometers; 12, pressure regulating device; 14, cooler; 15, cooling unit; 16, circulating pump; 17, sampling flask; 18, liquid air 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 [^{o}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:

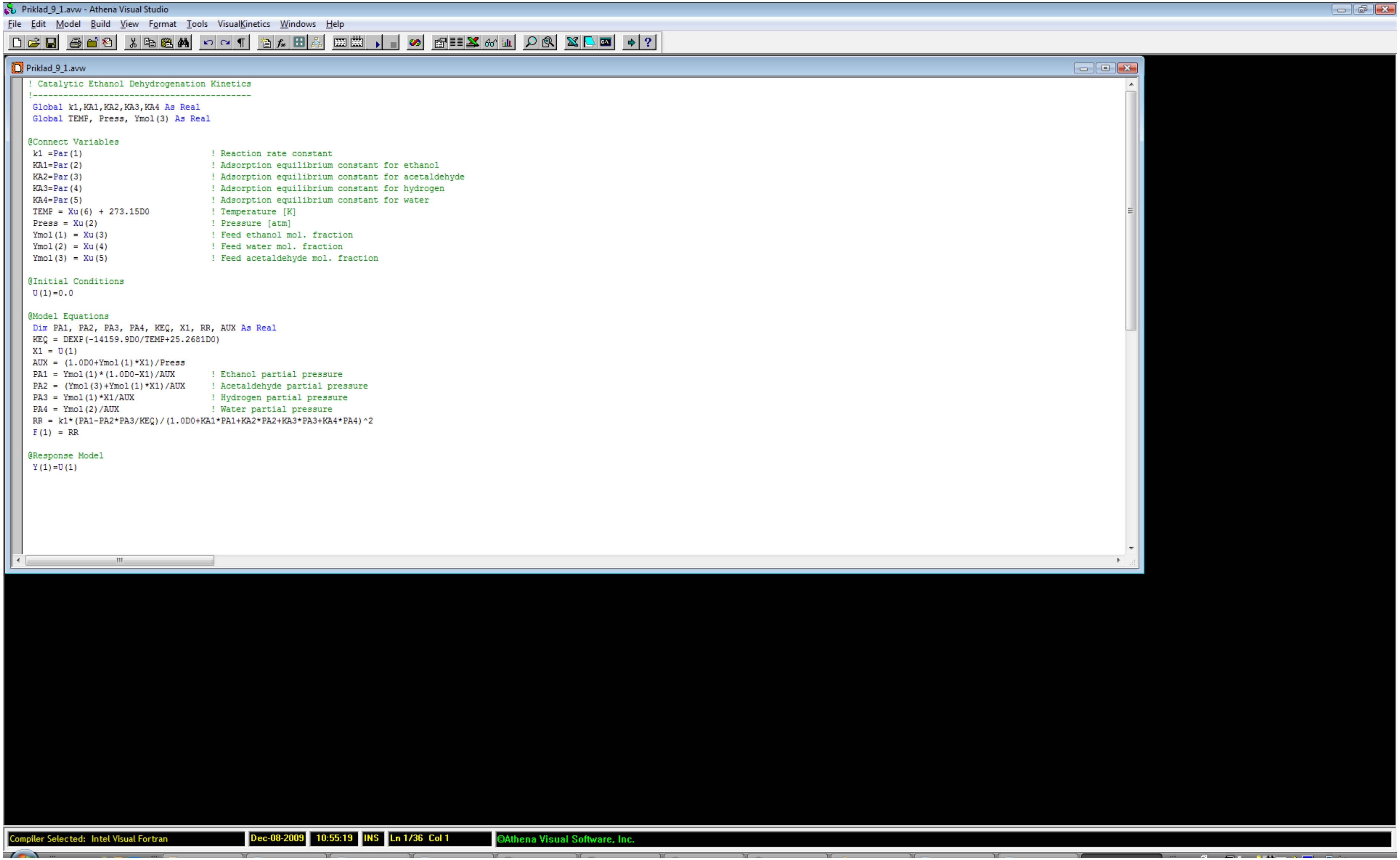
Minimize the objective function:

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

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

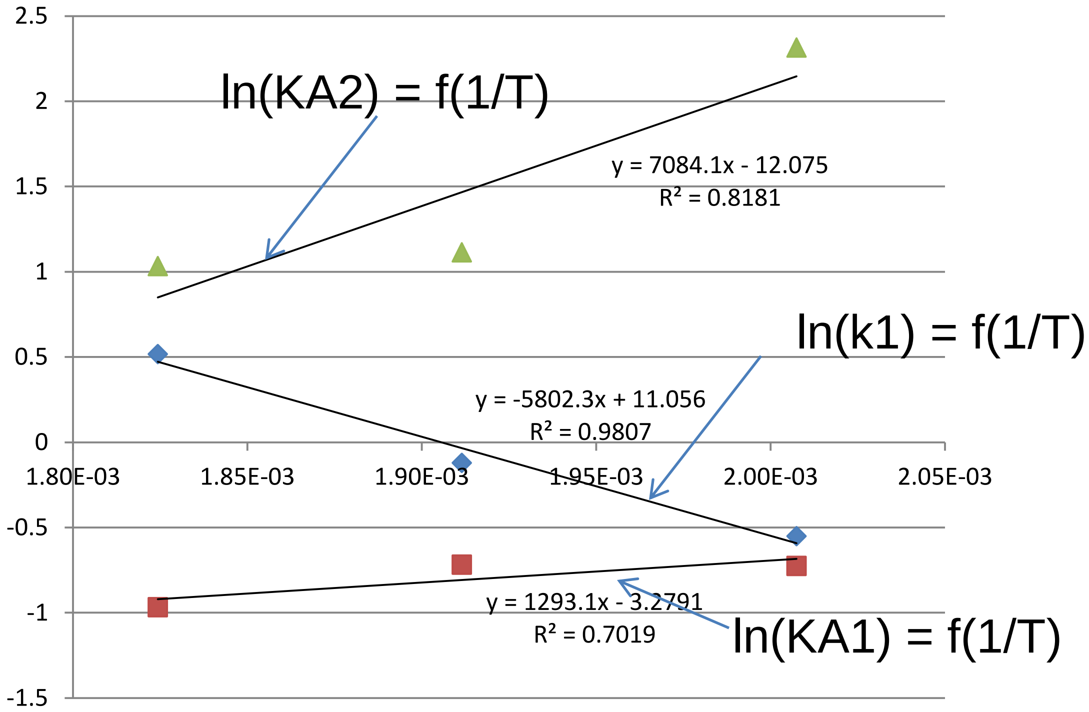
$$\frac{dX_1}{d\left(W / F_1^o\right)} = r_M(X_1) \qquad W / F_1^o = 0, X_1 = 0$$

ATHENA Visual Studio.



```
! 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)
```

	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

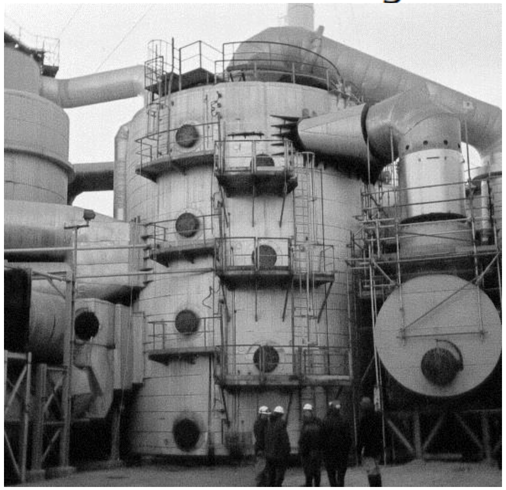


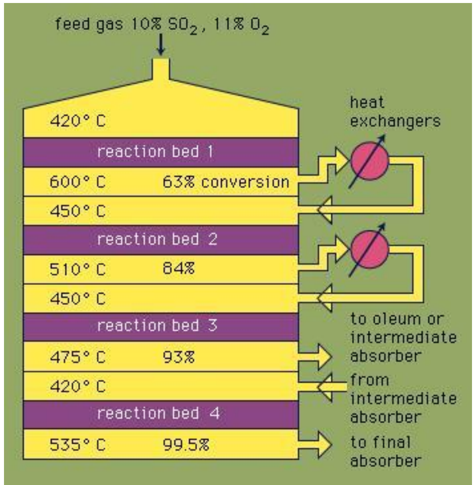
Fixed-bed catalytic reactors

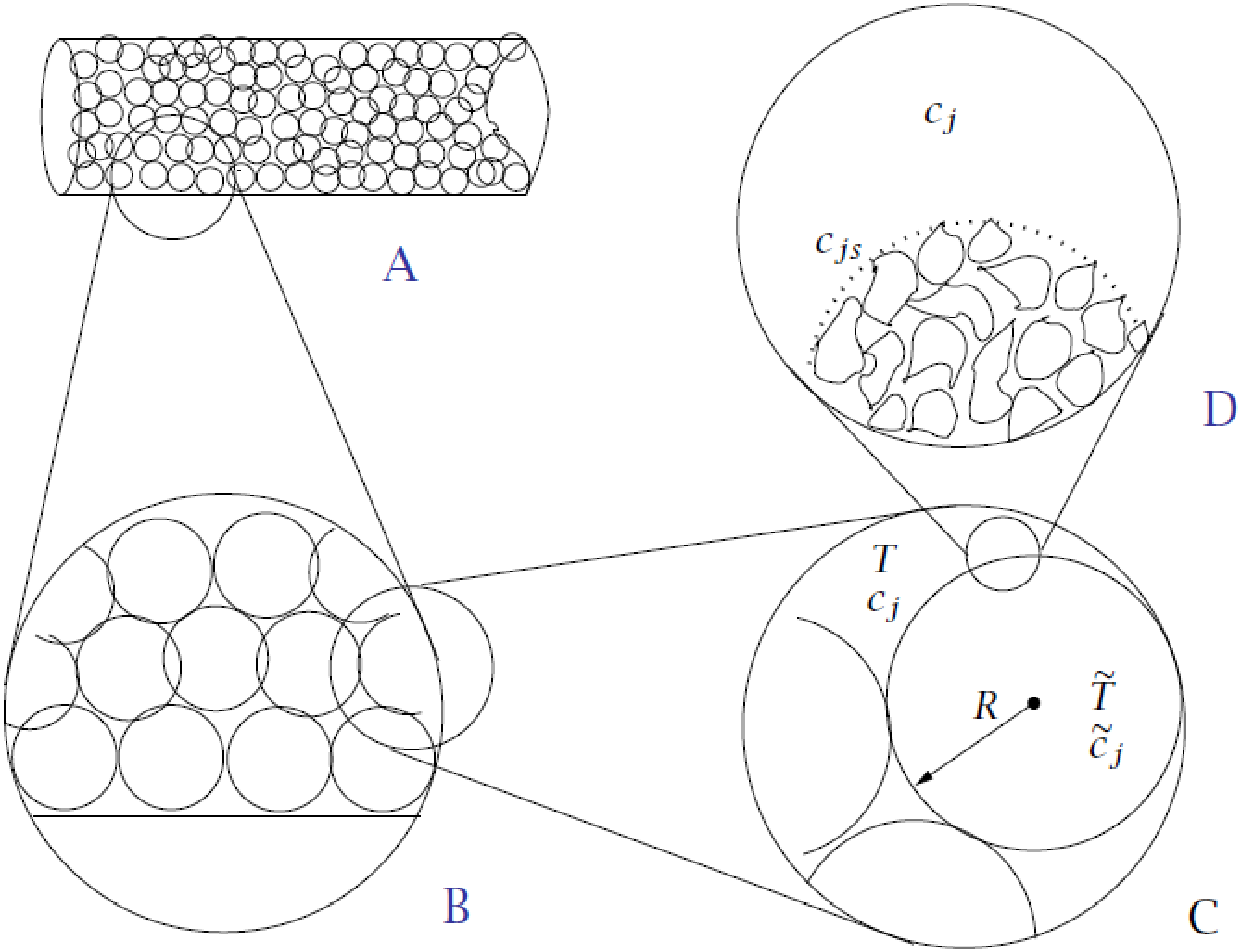
- In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame.

- 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.







Expanded views of a fixed bed reactor

The steps to consider

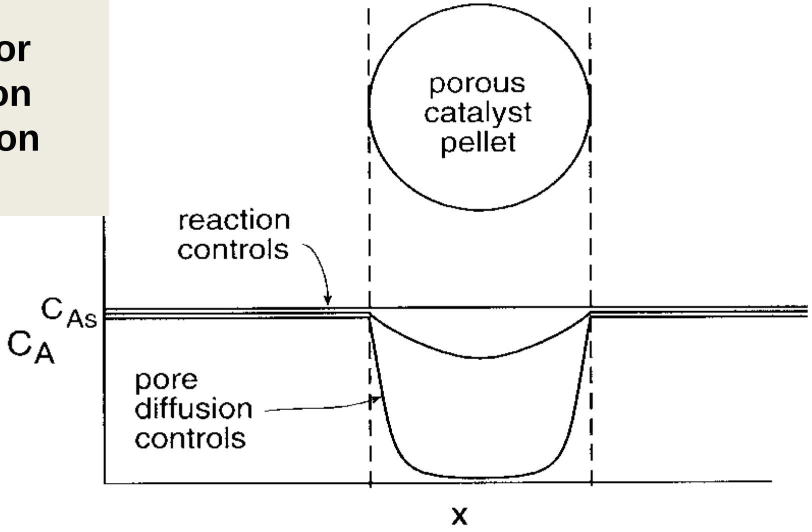
During any catalytic reaction the following steps occur:

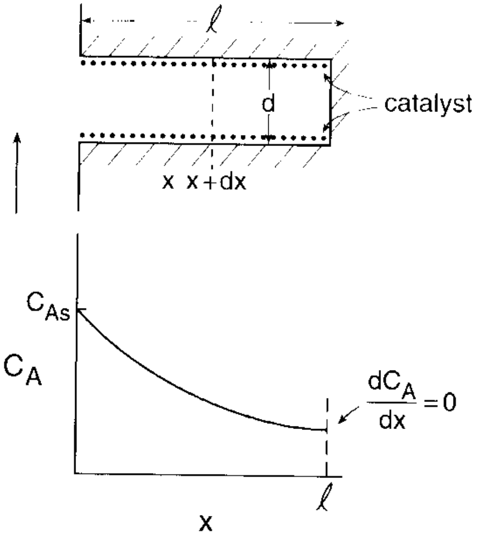
1. transport of reactants and energy from the bulk fluid up to the catalyst pellet exterior surface,
2. transport of reactants and energy from the external surface into the porous pellet,
3. adsorption, chemical reaction, and desorption of products at the catalytic sites,
4. transport of products from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

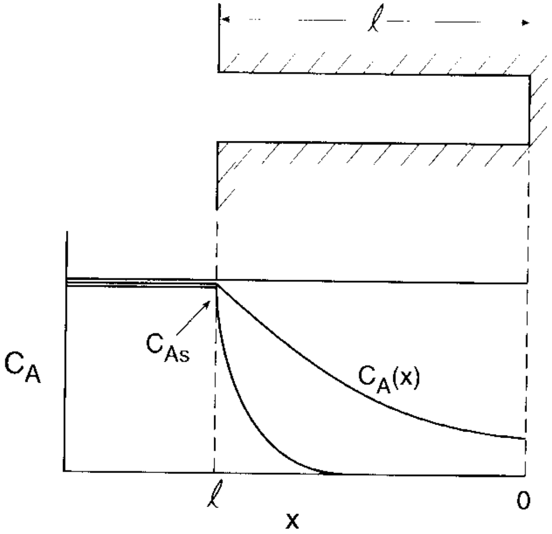
The coupling of transport processes with chemical reaction can lead to concentration and temperature gradients within the pellet, between the surface and the bulk, or both.

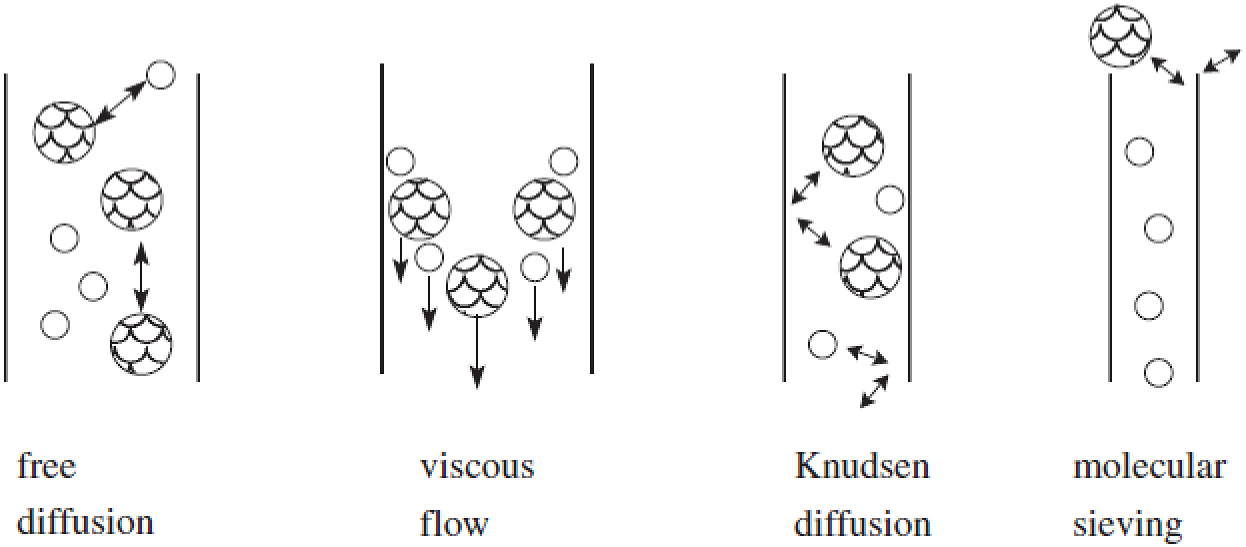
Internal mass transfer in a porous catalytic particle

Reactant concentration profiles within a porous catalyst pellet for situations where surface reaction controls and where pore diffusion affects reaction rate.








free diffusion
viscous flow
Knudsen diffusion
molecular sieving

Molecular diffusion

$$\vec{J}_i^D = -D_{i,m}\nabla c_i = -D_{i,m}\left(e_x\frac{\partial c_i}{\partial x} + e_y\frac{\partial c_i}{\partial y} + e_z\frac{\partial c_i}{\partial z}\right)$$ 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 $D_i^{K,e} = \frac{\varepsilon}{\tau}D_i^e$

Viscous (convective) flow

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

Total flow

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

First order gas phase reaction

$$A_{(g)} \rightarrow B_{(g)}$$

Reaction rate

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

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

$$x = L \qquad c_A = c_A^s$$

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

Solution

$$c_A(x) = B_1 e^{\alpha x} + B_2 e^{-\alpha x}$$
$$\alpha = \sqrt{\frac{4k_S}{d_p \overline{D}_A}}$$

$$c_A^s = B_1 e^{\alpha L} + B_2 e^{-\alpha L}$$
$$0 = B_1 - B_2$$
$$B_1 = B_2 = \frac{c_A^s}{e^{\alpha L} + e^{-\alpha L}}$$

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

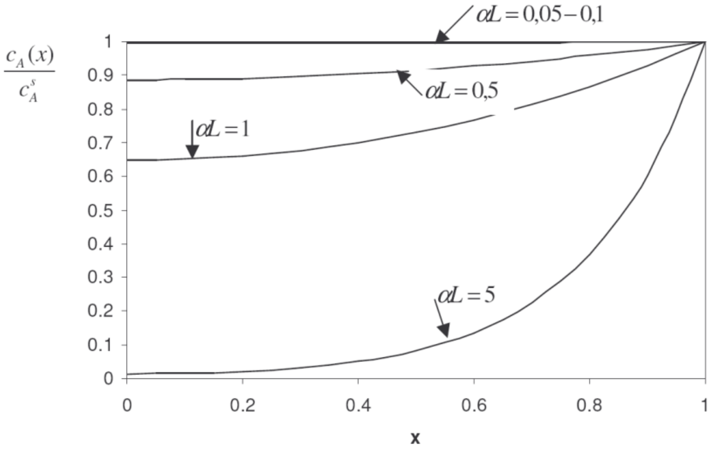
Mean reaction rate in the pore (rate of consumption of A)

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

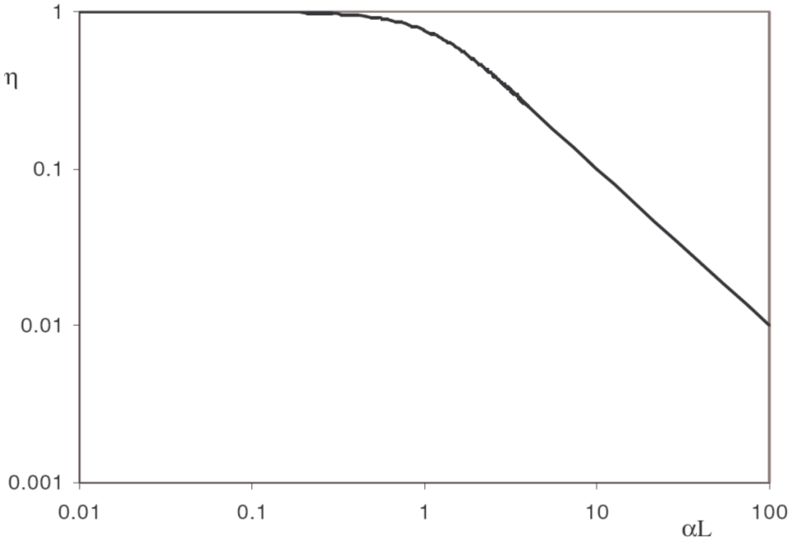
[mol A/s]

Effectiveness factor

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

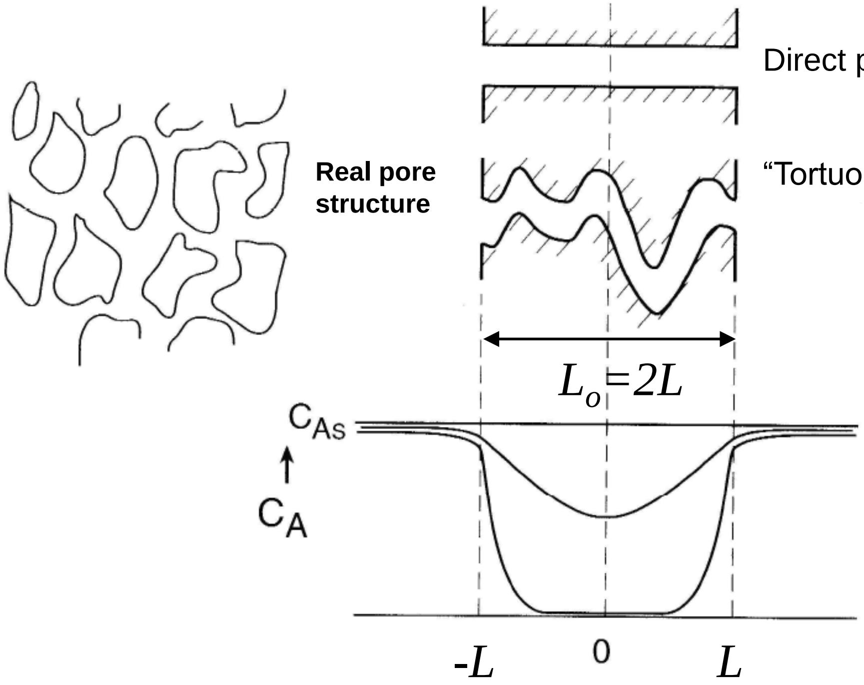


Concentration profiles of A in the pore



Effectiveness factor as a function of αL

Real catalytic particle of the shape of slab of the thickness L_o



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

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

$x = L \qquad c_A = c_A^s$

$x = 0 \qquad \dfrac{dc_A}{dx}=0$

Dimensionless variables

$$Y = \frac{c_A}{c_A^s} \qquad z = \frac{x}{L}$$

$$\frac{d^2Y}{dz^2} = \Phi^2 Y \qquad z = 0 \quad \frac{dY}{dz} = 0 \qquad z = 1 \quad Y = 1$$

$$\Phi = L\sqrt{\frac{S_g \rho k_S}{\overline{D}_A}}$$

Thiele number (module)

Solution

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

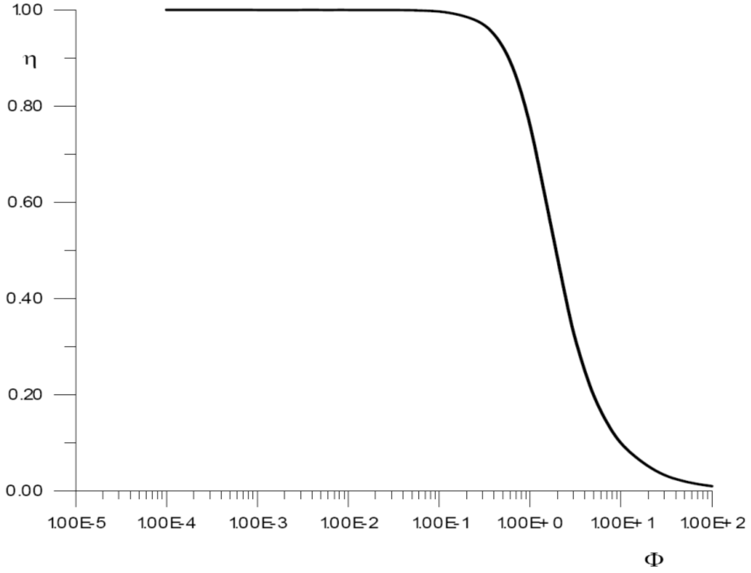
$$\eta = \qquad = \frac{2\rho\ \mathrm{S}\ \mathrm{S_g}\ \mathrm{k}\int_{\mathrm{o}}^{\mathrm{L}} \mathrm{c_A}\,dx}{2\rho\ \mathrm{S}\ \mathrm{LS_g}\ \mathrm{kc_A^o}} =$$

$$= \int_0^1 \frac{c_A}{c_A^o} d\left(\frac{x}{L}\right) = \int_0^1 Y dz = \frac{1}{\cosh(\Phi)} \int_0^1 \left[\cosh(\Phi z)\right] dz = \frac{1}{\Phi} \frac{\sinh(\Phi)}{\cosh(\Phi)} =$$

$$= \frac{tgh(\Phi)}{\Phi}$$

Real (measurable) reaction rate

$$\overline{R}_A = \eta\, 2\rho\, \mathrm{S}\ \mathrm{LS_g} k c_A^o = \frac{tgh(\Phi)}{\Phi} 2\rho\, \mathrm{S}\ \mathrm{LS_g} k c_A^o = \frac{tgh(\Phi)}{\Phi} m_{particle} S_g k c_A^o$$

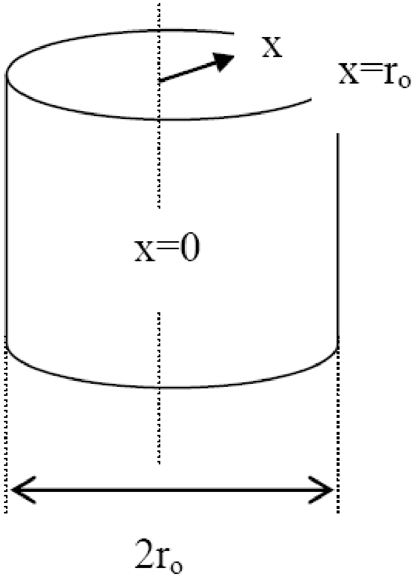


Effectiveness factor as a function of Thiele number

Cylinder

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

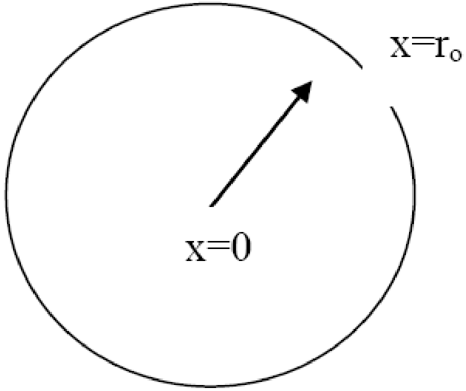
$$x=0 \qquad \frac{dc_A}{dx}=0 \qquad x=r_o \quad c_A=c_A^s$$



Sphere

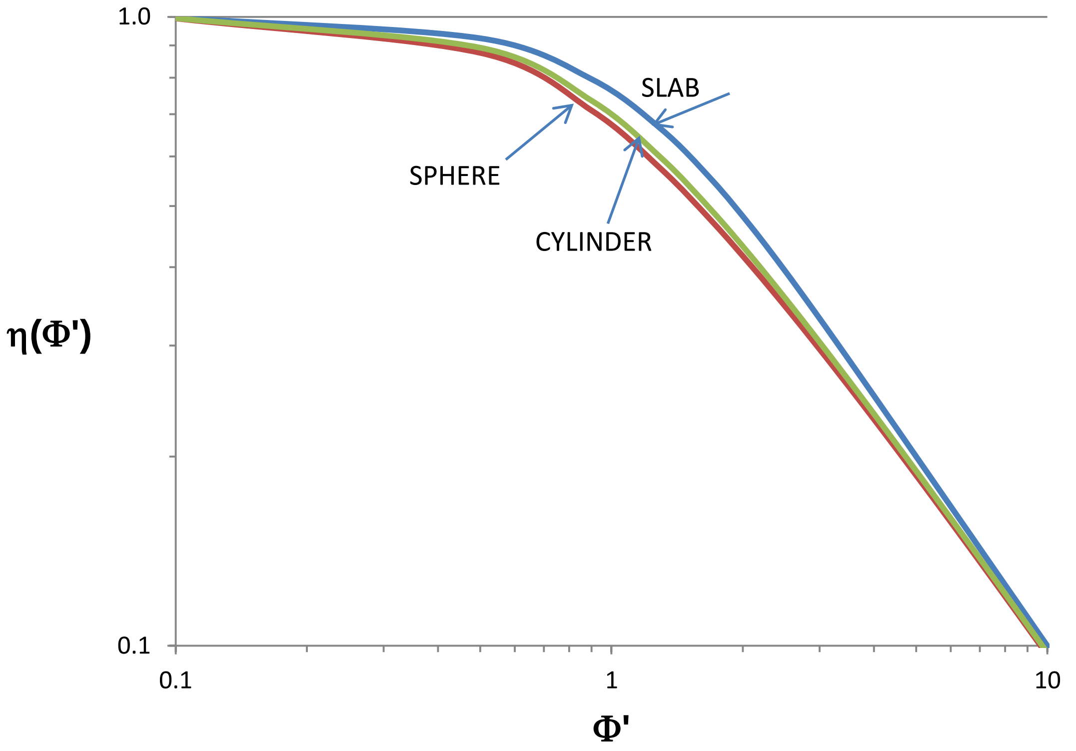
$$\overline{D}_{eA}\left[\frac{d^2c_A}{dx^2}+\frac{2}{x}\frac{dc_A}{dx}\right]=S_g\rho k_S c_A$$

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



Effectiveness factors for slab, cylinder and sphere

Shape	Effectiveness factor	Asymptote
Slab	$\eta = \frac{\tanh(\Phi)}{\Phi}, \Phi = \frac{L_o}{2}\sqrt{\frac{\rho_c k}{\bar{D}_1}}$	$\eta = \frac{1}{\Phi}, \Phi \geq 3$
Cylinder	$\eta = \frac{2}{\Phi}\frac{I_1(\Phi)}{I_o(\Phi)}$	$\eta = \frac{2}{\Phi}, \Phi \geq 6$
Sphere	$\eta = \frac{3}{\Phi}\left(\frac{1}{\tanh(\Phi)} - \frac{1}{\Phi}\right)$	$\eta = \frac{3}{\Phi}, \Phi \geq 9$



$$d = \frac{V_p}{A_p}, d = \frac{L}{2}\text{(slab)}, \; d = \frac{r_o}{2}\text{(cylinder)}, d = \frac{r_o}{3}\text{(sphere)}$$

$$\Phi' = d\sqrt{\frac{\rho S_g k}{\overline{D_{eA}}}} \qquad \eta = \text{tgh}(\Phi')/\Phi'$$

tgh(Φ'=tanh(Φ')

Exercise

The following first order gaseous catalytic reaction is conducted in a fixed bed reactor

$$N_2O_{(g)} \rightarrow N_{2(g)} + 1/2O_{2(g)}$$

$$r_M = k(T)P_{N_2O} \quad [\mathrm{mol/kg/s}]$$

The intrinsic rate constant for Fe-ZrO_2 catalyst is

$$k(T) = k_o exp\left[-\frac{E}{RT_{ref}}\left(\frac{T_{ref}}{T} - 1\right)\right]$$

where $k_o = 6.48\text{x}10^{-6}$ mol/(kg.s.Pa), T_{ref} = 773.15 K, E = 171.3 kJ/mol.

The feed consists of 2000 ppm N_2O in inert gaseous mixture at 8 bars, 1173 K, at total molar flow rate 715 mol/s. The catalyst is a spherical-shaped pellet with a radius of 5 mm. The pellet density is 5800 kg/m^3, the reactor bed porosity is 0.375. At 1173 K the effective diffusion coefficient of N_2O in porous pellet is $1.40\text{x}10^{-7}$ m^2/s. Determine the mass of catalyst required to achieve 90 % conversion of N_2O if the reactor is operated isothermally at 1173 K and 8 bars.

Solution

Effectiveness factor calculation

$$\bar{D}_A \frac{d^2 c_A}{dx^2} = \rho_{cat} k(T) RT c_A \Rightarrow \frac{d^2 Y_A}{dz^2} = \left(d^2 \frac{\rho_{cat} k(T) RT}{\bar{D}_A} \right) Y_A = \Phi'^2 Y_A$$

$$z = 0, \frac{dY_A}{dz} = 0$$

$$z = 1, Y_A = 1$$

$$\eta = \frac{tgh\left(\Phi'\right)}{\Phi'}$$

$$\Phi' = \frac{0.005}{3} \sqrt{\frac{5800 * 0.060289 * 8.314 * 1173}{1.4 * 10^{-7}}} = 8225.67 \Rightarrow \eta = 1.2157 * 10^{-4}$$

Mass of catalyst

$$F_A^o \frac{dX_A}{dW} = \eta k(T) P y_{g,A} = \eta k(T) P \frac{F_A}{F} = \eta k(T) P \frac{F_A^o (1 - X_A)}{F}$$

$$W = \frac{F}{\eta k(T) P} \int_0^{0.9} \frac{dX_A}{1 - X_A} = \frac{715}{1.2157 * 10^{-4} * 0.060289 * 8.0 * 10^5} \left(-\ln\left(0.1\right) \right) \cong 122 \text{ kg}$$

Internal and external mass transfer

$$\bar{D}_A \frac{d^2 c_A}{dx^2} = S_g \rho k_S c_A$$

$$x = l \qquad -\bar{D}_A \frac{dc_A}{dx} = k_{cA}(c_A^s - c_A^o)$$

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

Dimensionless variables $Y = \frac{c_A}{c_A^o}$ $z = \frac{x}{l}$ we get

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

$$z = 1 \qquad -\frac{dY}{dz} = Bi_{mA}(Y(z=1) - 1)$$

$$z = 0 \qquad \frac{dY}{dz} = 0$$

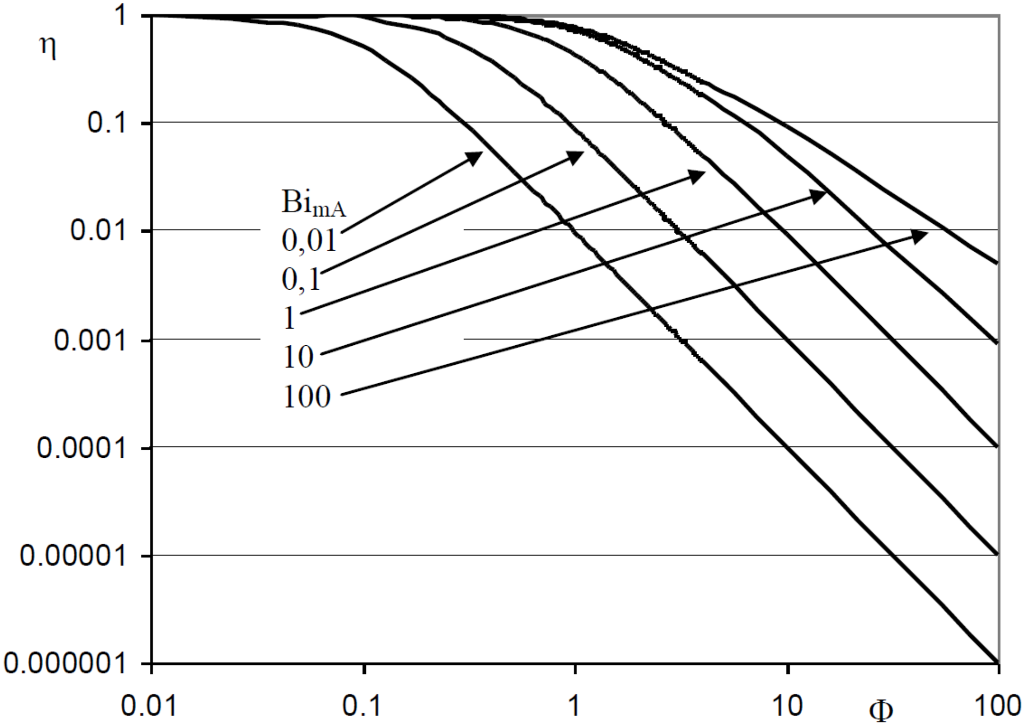
Dimensionless parameter Bi_{mA} – Biot number for mass transfer

$$Bi_{mA} = \frac{k_{cA} l}{\bar{D}_A}$$

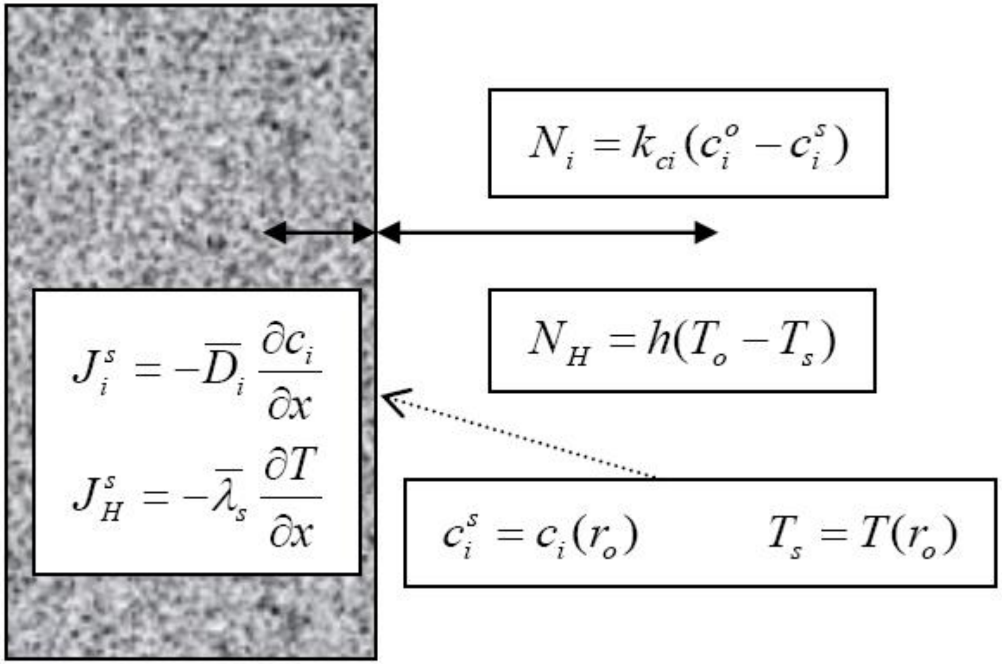
Solution of differential equation has the form:

$$Y(z) = \frac{\cosh(\Phi z)}{\cosh(\Phi) + \frac{\Phi}{Bi_{mA}} \sinh(\Phi)}$$

$$\eta = \frac{1}{\Phi} \frac{\sinh(\Phi)}{\cosh(\Phi) + \frac{\Phi}{Bi_{mA}} \sinh(\Phi)} = \frac{1}{\Phi} \frac{\tanh(\Phi)}{1 + \frac{\Phi}{Bi_{mA}} \tanh(\Phi)}$$



Heat and mass transfer



$$N_i = k_{ci}(c_i^o - c_i^s)$$

$$J_i^s = -\overline{D}_i \frac{\partial c_i}{\partial x}$$

$$J_H^s = -\overline{\lambda}_s \frac{\partial T}{\partial x}$$

$$N_H = h(T_o - T_s)$$

$$c_i^s = c_i(r_o) \qquad T_s = T(r_o)$$

Balance equations

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

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

a = 0 Slab
1 Cylinder
2 Sphere

Boundary conditions

$x = 0$

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

$x = r_o$

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

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

Maximal temperature gradient in particle of catalyst(Prater 1958)

Elimination of r_V from enthalpy balance:

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

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

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

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

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

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

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

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

Chemical Engineering Science, 1958, Vol 8, pp 284 to 286 Pergamon Press Ltd

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

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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 *cyclo*hexane 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 *cyclo*hexane 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 Teilchengeometrie ist Für die Anwendung dieser Gleichung werden als Beispiele die Dehydrierung von *Cyclo*hexan 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 :—

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

where T is the centigrade temperature at all points within the particle which have a concentration of reactant c (mole/cm^3)

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/cm^3)

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

D_e is the effective diffusivity of the particle (cm^2/sec)

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

DAMKÖHLER [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

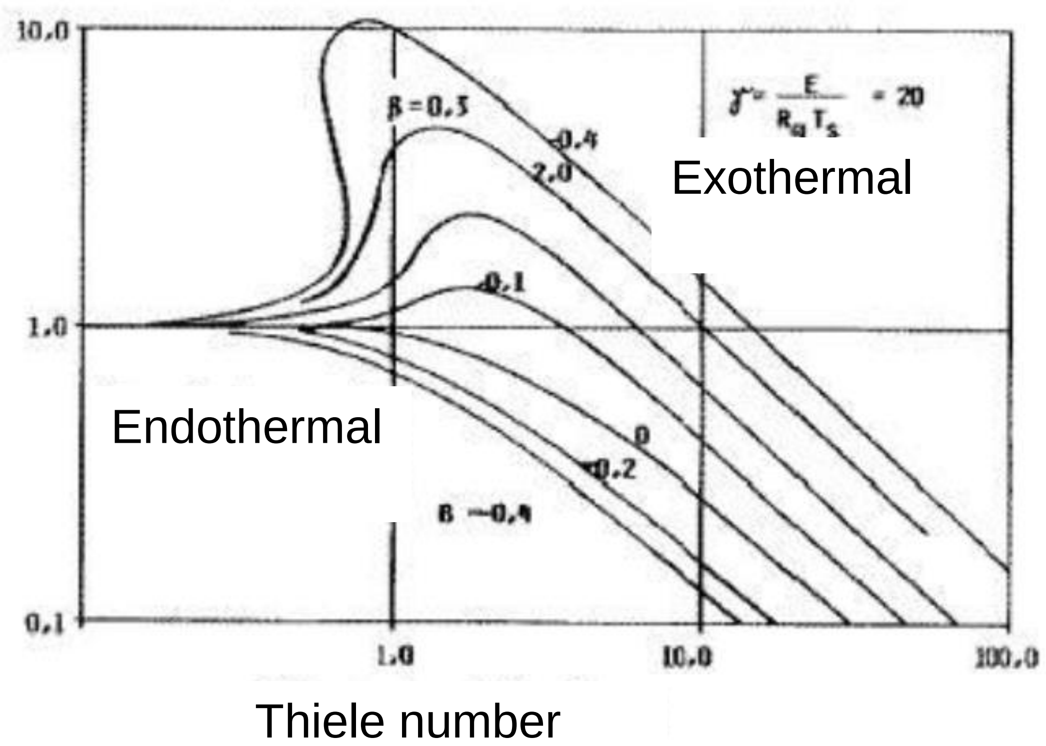
The next reaction to be considered is the dehydrogenation of *cyclo*hexane over a commercial platinum-alumina reforming catalyst. This is an endothermic reaction with a ΔH of $+ 52.54 \times 10^3$ cal/mole at 400°C. The conditions are 400°C reaction temperature, 4 : 1 hydrogen to hydrocarbon ratio and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

$$D_e = 15.6 \times 10^{-3} \text{ cm/sec}^2 \text{ (\textit{cyclo}hexane at 400°C)}$$

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

The value of the equilibrium concentration of *cyclo*hexane 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

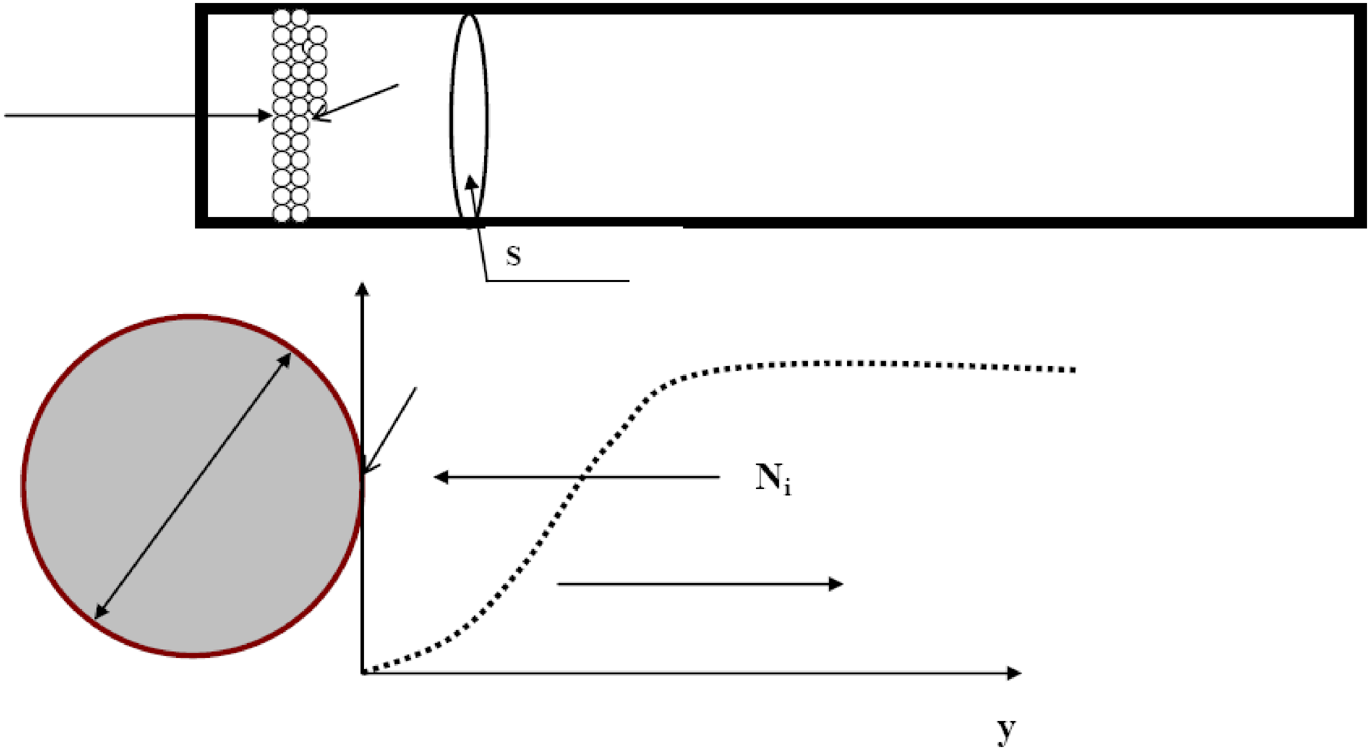
SUMMARY

1. The kinetics of heterogeneous catalytic reaction can be described on the basis Langmuir model of ideal catalytic surface using sequence of both mass (and heat) transfer and elementary reaction steps.
2. The kinetic model has to be confronted with experimental data and the kinetic parameters (kinetic and adsorption constants) have to be estimated.
3. Mass and heat transfer have important impact on overall reaction rate and the models involving mass and heat transfer mechanisms should be formulated and solved.
4. Mass transfer in porous structure of catalytic pellet is complex phenomena and depends on pore size (distribution of pore size), interactions between fluid molecules and pore wall, transport parameters of fluid (diffusion coefficients, viscosity, heat conductivity) and solid phase, also on the hydrodynamics of surrounding fluid flow (external and internal mass transfer).

Models of catalytic reactors

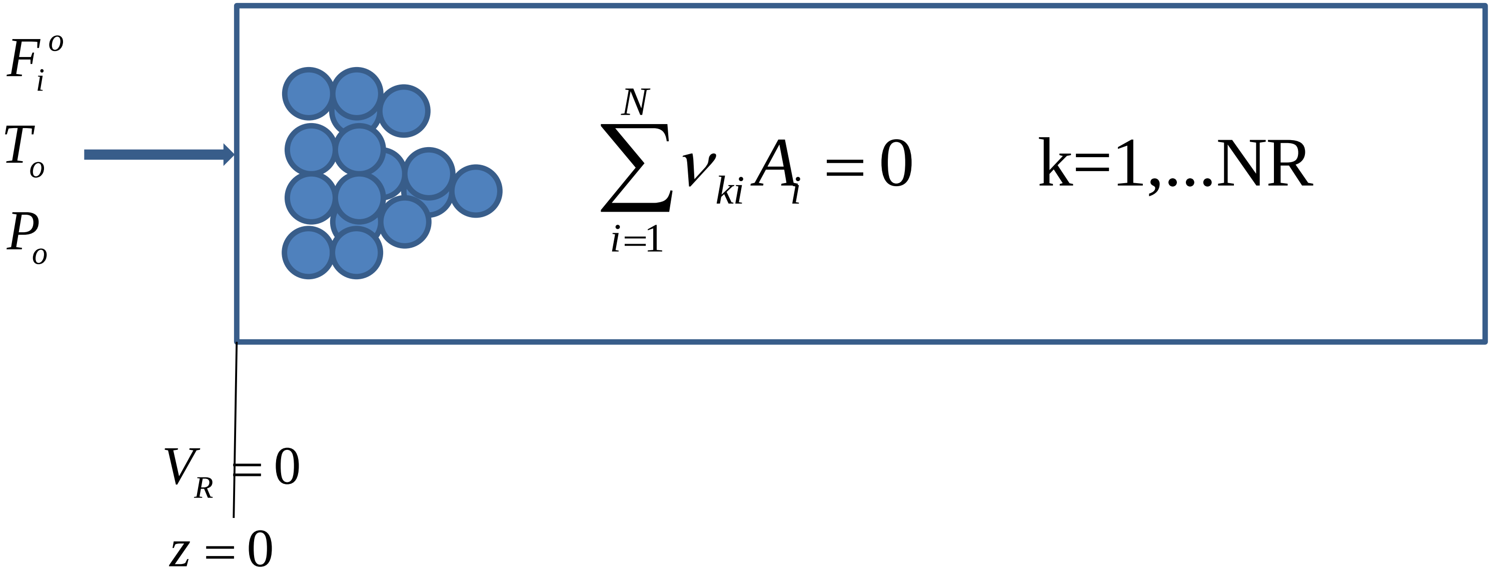
Model equations involve:

- 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	• withou 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



F_i^o

T_o

P_o

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

$V_R = 0$

$z = 0$

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.

$$\frac{\mathrm{d}F_i}{\mathrm{d}z} = S_R \rho_b \sum_{k=1}^{NR} \nu_{ki} r_{M,k}$$

$$F c_p \frac{\mathrm{d}T}{\mathrm{d}z} = S_R \left[\rho_b \sum_{k=1}^{NR} \left(-\Delta_r H_k\right) r_{M,k} + \frac{4}{d_R}\,\omega\left(T_m - T\right)\right]$$

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\left[150 \frac{\mu_f}{d_p^2}\frac{\left(1-\varepsilon_b\right)^2}{\varepsilon_b^3}\,\mathrm{v}_f^o + 1.75 \frac{\rho_f}{d_p}\frac{\left(1-\varepsilon_b\right)}{\varepsilon_b^3}\left(\mathrm{v}_f^o\right)^2\right]$$

$$z = 0, F_i = F_i^o, T = T_o, P = P_o$$

μ_f - fluid dynamic viscosity (Pa.s)
ρ_f - fluid density (kg/m^3)
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/m^3)
S_R – (empty) reactor cross section area (m^2)

↓

Numerical solution gives $F_i(z), T(z), P(z)$

Example

Consider the oxidation of CO and C_3H_6 in a catalytic converter containing spherical catalyst pellets with particle radius 0.175 cm (0.05 mass % Pt on Al_2O_3). The initial composition of gas mixture is 2 % mol CO, 3 % O_2, 0.05 % C_3H_6 + N_2, 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/m^3. The reactions of interest are

$$\mathrm{CO_{(g)}} + \frac{1}{2}\mathrm{O_{2(g)}} \rightarrow \mathrm{CO_{2(g)}}$$

$$\mathrm{C_3H_{6(g)}} + \frac{9}{2}\mathrm{O_{2(g)}} \rightarrow 3\mathrm{CO_{2(g)}} + 3\mathrm{H_2O_{(g)}}$$

$$r_{M,1} = \frac{k_1(T)\, c_{O_2} c_{CO}}{\left(1 + K_{CO} c_{CO} + K_{\mathrm{C_3H_6}} c_{\mathrm{C_3H_6}}\right)^2} \qquad \mathrm{mol/g/s}$$

$$r_{M,2} = \frac{k_2(T)\, c_{O_2} c_{\mathrm{C_3H_6}}}{\left(1 + K_{CO} c_{CO} + K_{\mathrm{C_3H_6}} c_{\mathrm{C_3H_6}}\right)^2} \qquad \mathrm{mol/g/s}$$

$$k_1(T) = 7.07 \times 10^{19} \exp\left[-\frac{13106}{T}\right] \qquad \mathrm{cm^6/(molgs)}$$

$$k_2(T) = 1.47 \times 10^{21} \exp\left[-\frac{15109}{T}\right] \qquad \mathrm{cm^6/(molgs)}$$

$$K_{CO} = 8.099 \times 10^{6} \exp\left[\frac{409}{T}\right] \qquad \mathrm{cm^3/mol}$$

$$K_{\mathrm{C_3H_6}} = 2.579 \times 10^{8} \exp\left[-\frac{191}{T}\right] \qquad \mathrm{cm^3/mol}$$

Oh, S.H., Cavenish J.C., Hegedus L.L., AICHE J. 26 (1980) 935.

Data from http://webbook.nist.gov/chemistry/:

$c_{p,i}(750\text{ K}):$

$c_{p,CO} = 31.5\quad \text{J/mol/K} \quad \Delta\text{H}_{f,298.15} = -110.53\text{ kJ/mol}$

$c_{p,O_2} = 33.4\quad \text{J/mol/K}$

$c_{p,CO_2} = 50.0\quad \text{J/mol/K} \quad \Delta\text{H}_{f,298.15} = -393.52\text{ kJ/mol}$

$c_{p,N_2} = 31.1\quad \text{J/mol/K}$

$c_{p,C_3H_6} = 123.9\quad \text{J/mol/K} \quad \Delta\text{H}_{f,298.15} = 20.41\text{ kJ/mol}$

$c_{p,H_2O} = 38.12\quad \text{J/mol/K} \quad \Delta\text{H}_{f,298.15} = -241.83\text{ kJ/mol}$

Viscosity of $\text{N}_{2(g)}$ at 750 K:

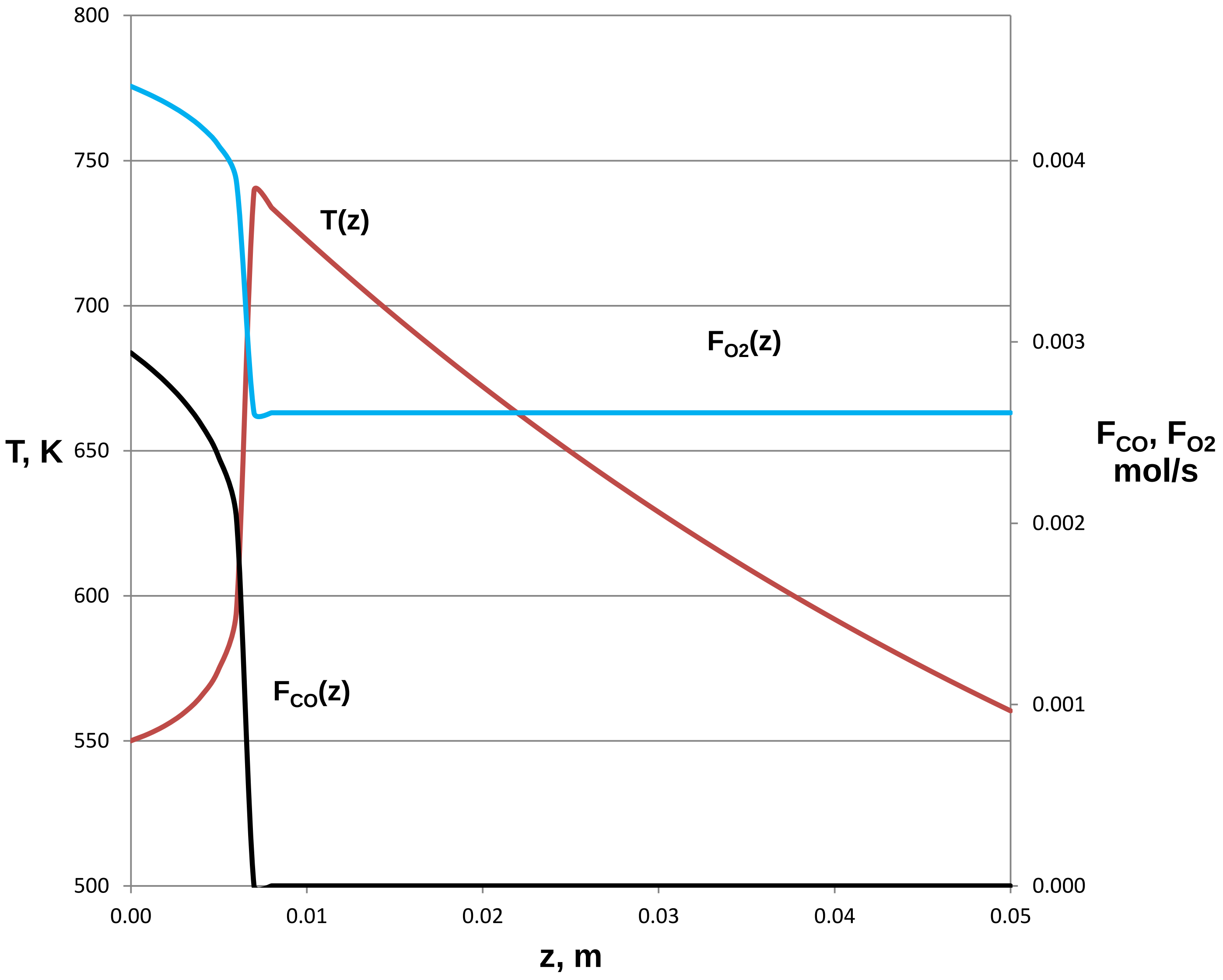
$\mu_f = 3.44\times10^{-5}\ \text{Pa.s}$

Data supplement:

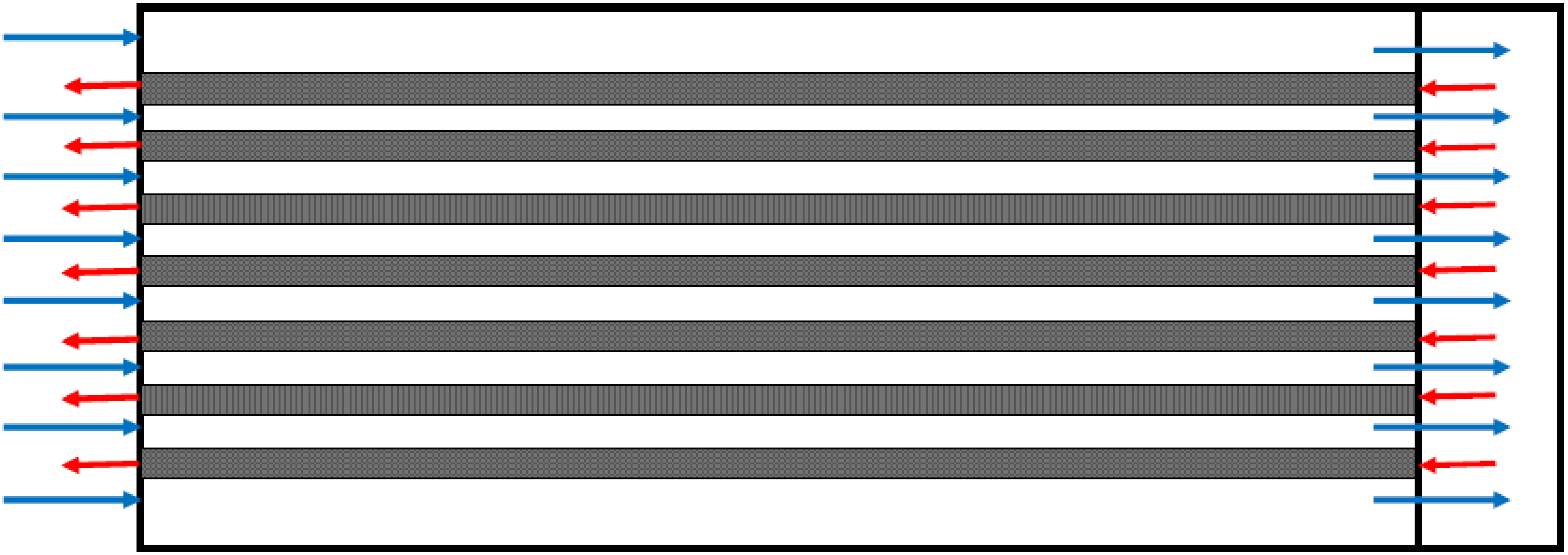
$\omega = 230\text{ W/(m}^2\text{K)} \qquad T_m = 325\text{ K}$

$T_o = 500\text{ K} \qquad P_o = 202\text{ kPa}$

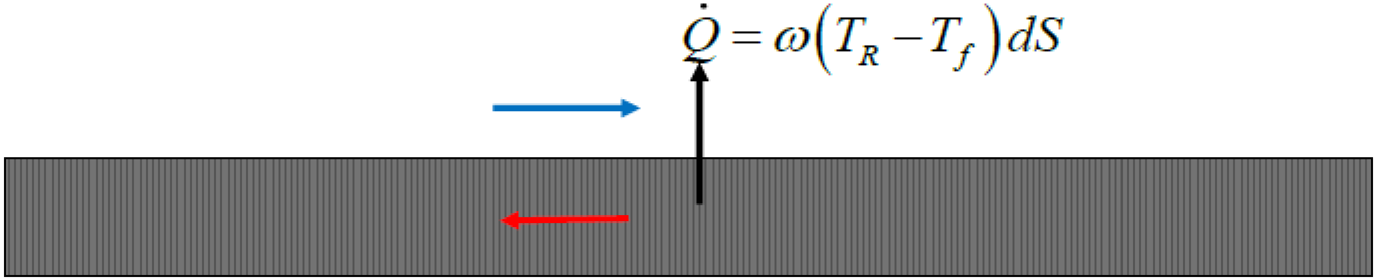
Numerical integration done by SIRK42E



Discussion: internal x external mass and heat transfer



The counter-current catalytic reactor for ammonia synthesis is depicted on above presented figure. The cold gas mixture (21.75 mol. % N_2 , 65.25 mol. % H_2 , 5 mol. % NH_3 , 4 mol. % CH_4 a 4 mol. % Ar) is introduced into the shell side (blue arrows) and is preheated by the heat transferred from catalytic tubes.



$$\dot{Q} = \omega\left(T_R - T_f\right)dS$$

Synthesis of ammonia is based on the high pressure gas phase catalytic reaction

$$N_2 \;+\; 3\,H_2 \rightarrow 2\,NH_3$$

Kinetics of ammonia synthesis on Fe catalyst (Apelbaum, Temkin, 1940)

$$r_V = k_f \frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - k_b \frac{p_{NH_3}}{p_{H_2}^{1.5}} \qquad \left[\mathrm{kmol/m^3/hr}\right]$$

$$k_f = 9.88469 \times 10^5 \exp\left(-\frac{87085}{R\,T}\right) \qquad \left[\mathrm{kmol/m^3/hr/bar^{1.5}}\right]$$

$$k_b = 6.751949 \times 10^{15} \exp\left(-\frac{198454}{R\,T}\right) \qquad \left[\mathrm{kmol \times bar^{0.5}/m^3/hr}\right]$$

$$R = 8.31446 \;\; \mathrm{J/mol/K}$$

1. Formulate the molar and enthalpy balances for 1-D plug flow pseudohomogeneous catalytic reactor model.
2. Calculate the concentration and temperature profiles in the catalytic tubes and shell using 1-D plug flow pseudohomogeneous catalytic reactor model. Constant pressure (no pressure drop) is assumed.

Data

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	ω=2093 kJ/m^2/hr/K=2096×10^3 / 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]

The enthalpy of reaction and the 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.

Solution of boundary value problem by shooting method

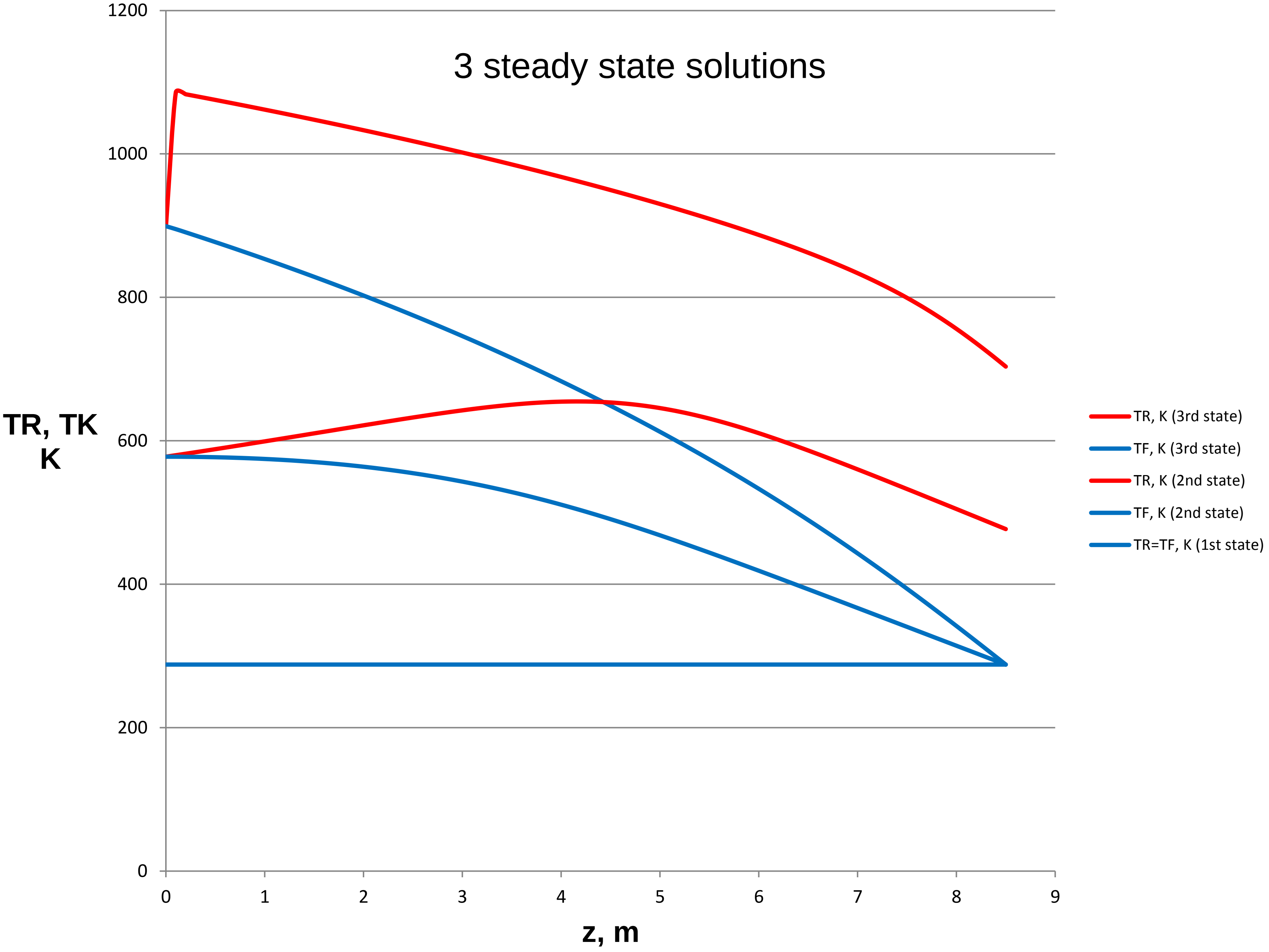
$$\frac{dF_i}{dz} = N_t S_t \nu_i r_V$$

$$\frac{dT_R}{dz} = \frac{N_t S_t}{\sum_{i=1}^{NC} F_i c_{pi}(T_R)} \left[(-\Delta_r H) r_V + \frac{4\omega}{d_t}(T_F - T_R) \right]$$

$$\frac{dT_F}{dz} = \frac{N_t \pi d_t \omega}{\sum_{i=1}^{NC} F_i^o c_{pi}(T_F)} (T_F - T_R)$$

$$z = 0, F_i = F_i^o, T_R = T_F$$

$$z = L, T_F = T_F^o$$

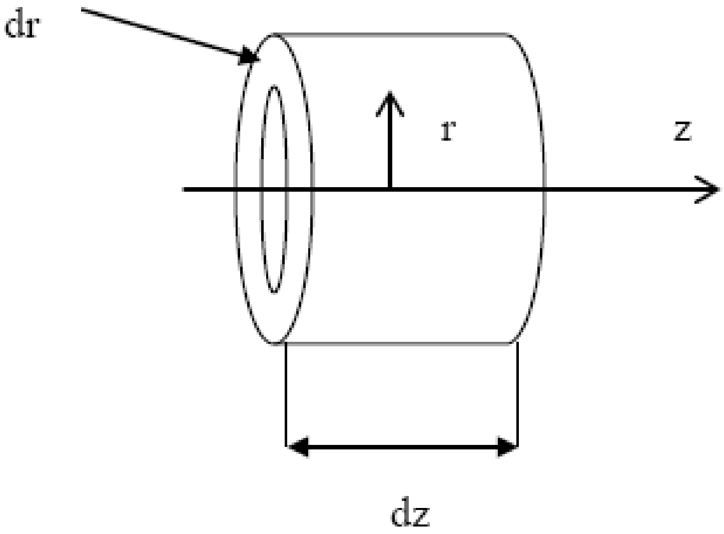

3 steady state solutions
TR, TK
K
1200
1000
800
600
400
200
0
0
1
2
3
4
5
6
7
8
9
z, m
TR, K (3rd state)
TF, K (3rd state)
TR, K (2nd state)
TF, K (2nd state)
TR=TF, K (1st state)

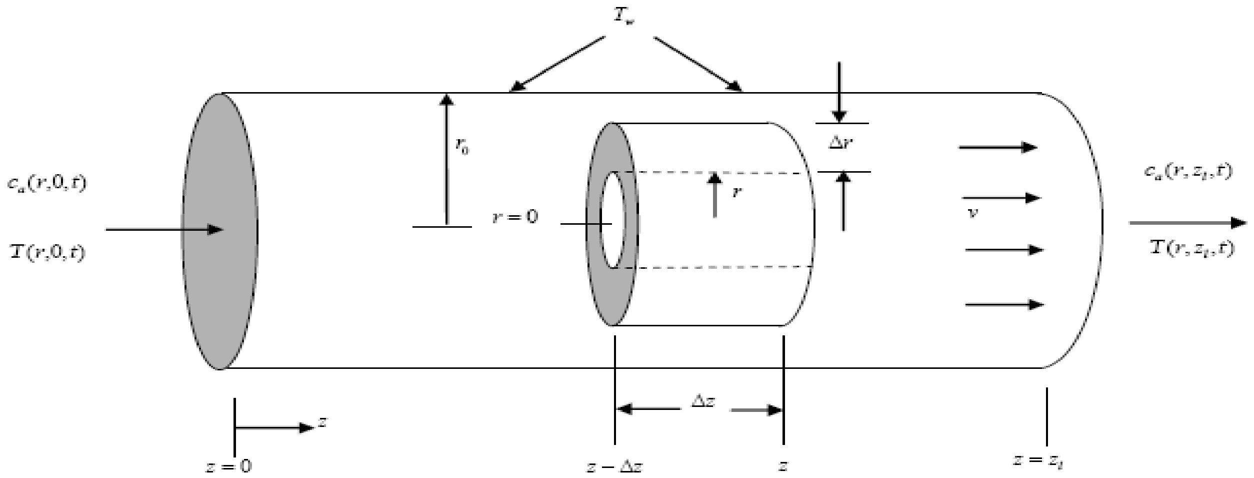
2-D pseudo homogeneous model with axial and radial dispersion

$$N_i = -D_{ai}\frac{\partial c_i}{\partial z} - D_{ri}\frac{\partial c_i}{\partial r} + y_i\sum_{j=1}^{NS} N_j = -D_{ai}\frac{\partial c_i}{\partial z} - D_{ri}\frac{\partial c_i}{\partial z} + c_i.\mathrm{v}$$

$$N_H = -\lambda_{am}\frac{\partial T}{\partial z} - \lambda_{rm}\frac{\partial T}{\partial r} + \mathrm{v}\rho_g c_{pm} T$$

Balance element of volume





Balance equations

$$D_{ri}\left(\frac{\partial^2 c_i}{\partial r^2}+\frac{1}{r}\frac{\partial c_i}{\partial r}\right)+D_{ai}\frac{\partial^2 c_i}{\partial z^2}-\mathrm{v}_s\frac{\partial c_i}{\partial z}+\nu_i r_V=0$$

$$\lambda_{rm}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)+\lambda_{am}\frac{\partial^2 T}{\partial z^2}-\mathrm{v}_s\rho_g c_{pm}\frac{\partial T}{\partial z}+(-\Delta H_r)r_V=0$$

Boundary and initial conditions

$$z=0, \qquad 0<r<r_o$$

$$-D_{ai}\frac{\partial c_i}{\partial z}+\nu c_i=\nu c_i^o$$

$$-\lambda_{am}\frac{\partial T}{\partial z}+\nu\rho_g c_{pm}T=\nu\rho_g c_{pm}T_o$$

$$r=r_o$$

$$\frac{\partial c_i}{\partial r}=0 \qquad -\lambda_{\mathrm{rm}}\frac{\partial T}{\partial r}=h_w(T-T_m)$$

$$r=0$$

$$\frac{\partial c_i}{\partial r}=0 \qquad \frac{\partial T}{\partial r}=0$$