

8. Heterogeneous reaction

• 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

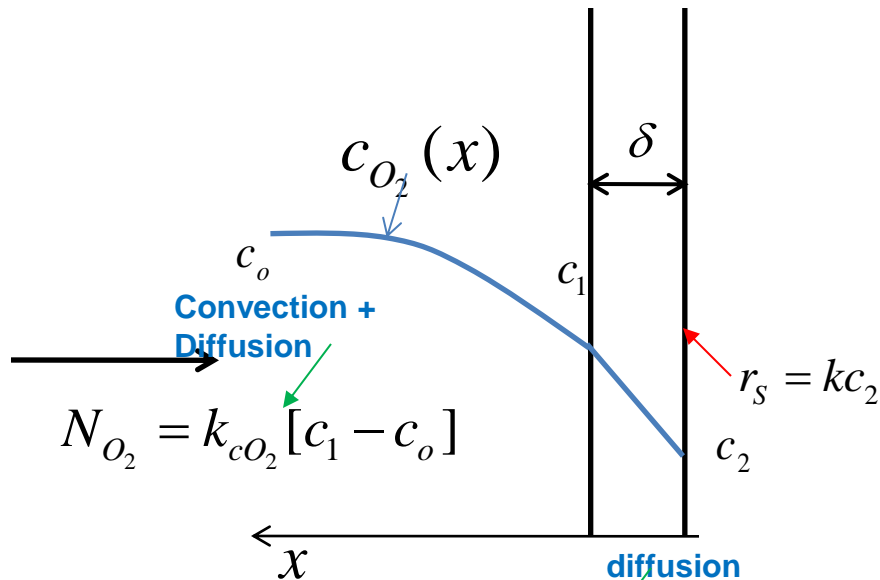
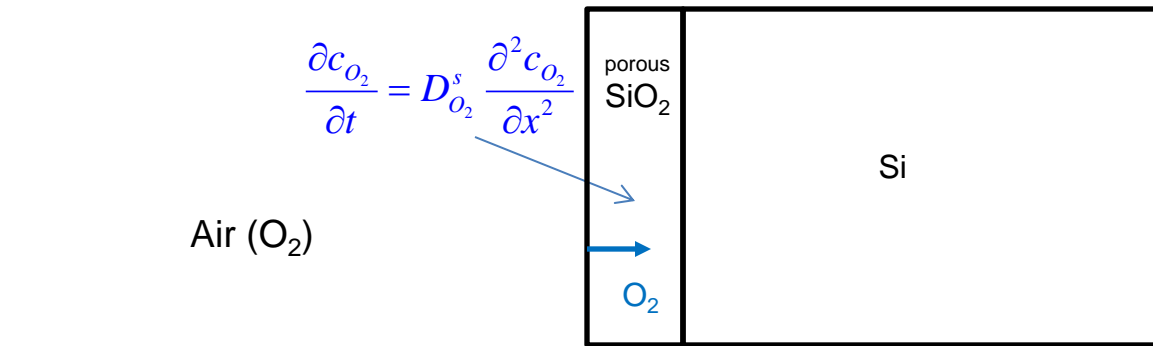
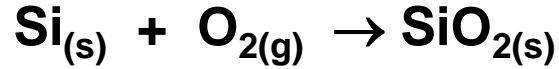
- Dissolution with chemical reaction
 $\text{Cl}_{2(s)} + 2\text{NaOH}_{(l)} \rightarrow \text{NaOCl}_{(l)} + \text{NaCl}_{(l)} + \text{H}_2\text{O}_{(l)}$
 $3\text{NO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{HNO}_{3(l)} + \text{NO}_{(g)}$

• 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.

Example



N_{O_2} flux density of O_2 in gas phase ($\text{mol.m}^{-2}.\text{s}^{-1}$)

$J_{O_2}^{(D)}$ flux density of O_2 in SiO_2 layer ($\text{mol.m}^{-2}.\text{s}^{-1}$)

k_{cO_2} coefficient of mass transfer of O_2 (m.s^{-1})

$D_{O_2}^s$ diffusion coefficient of O_2 in SiO_2 ($\text{m}^2.\text{s}^{-1}$)

r_s rate of chemical reaction ($\text{mol. m}^{-2}.\text{s}^{-1}$)

$$J_{O_2}^{(D)} = -D_{O_2}^s \frac{dc_{O_2}}{dx} \cong D_{O_2}^s \frac{[c_2 - c_1]}{\delta}$$

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 :

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

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

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

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

SiO₂ layer thickness and Si conversion :

reaction rate

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

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

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

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

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

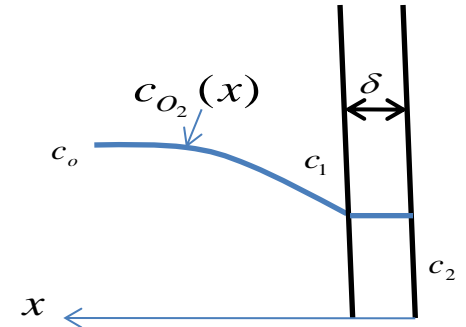
$M_{SiO_2}, M_{Si}, \rho_{SiO_2}, \rho_{Si}$ Molar weights and densities of SiO₂ a Si

δ_o Initial thickness of Si slab

3 limiting cases

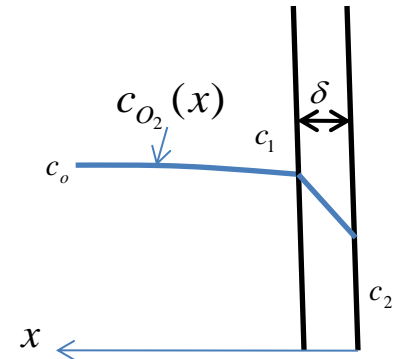
1. Rate determining step is the external mass transfer of oxygen towards interface (gas - SiO₂)

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



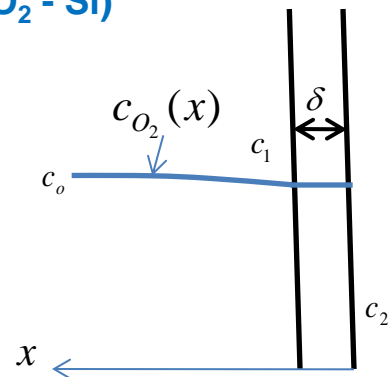
2. Rate determining step is the internal mass transfer of oxygen in porous SiO₂ layer

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



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

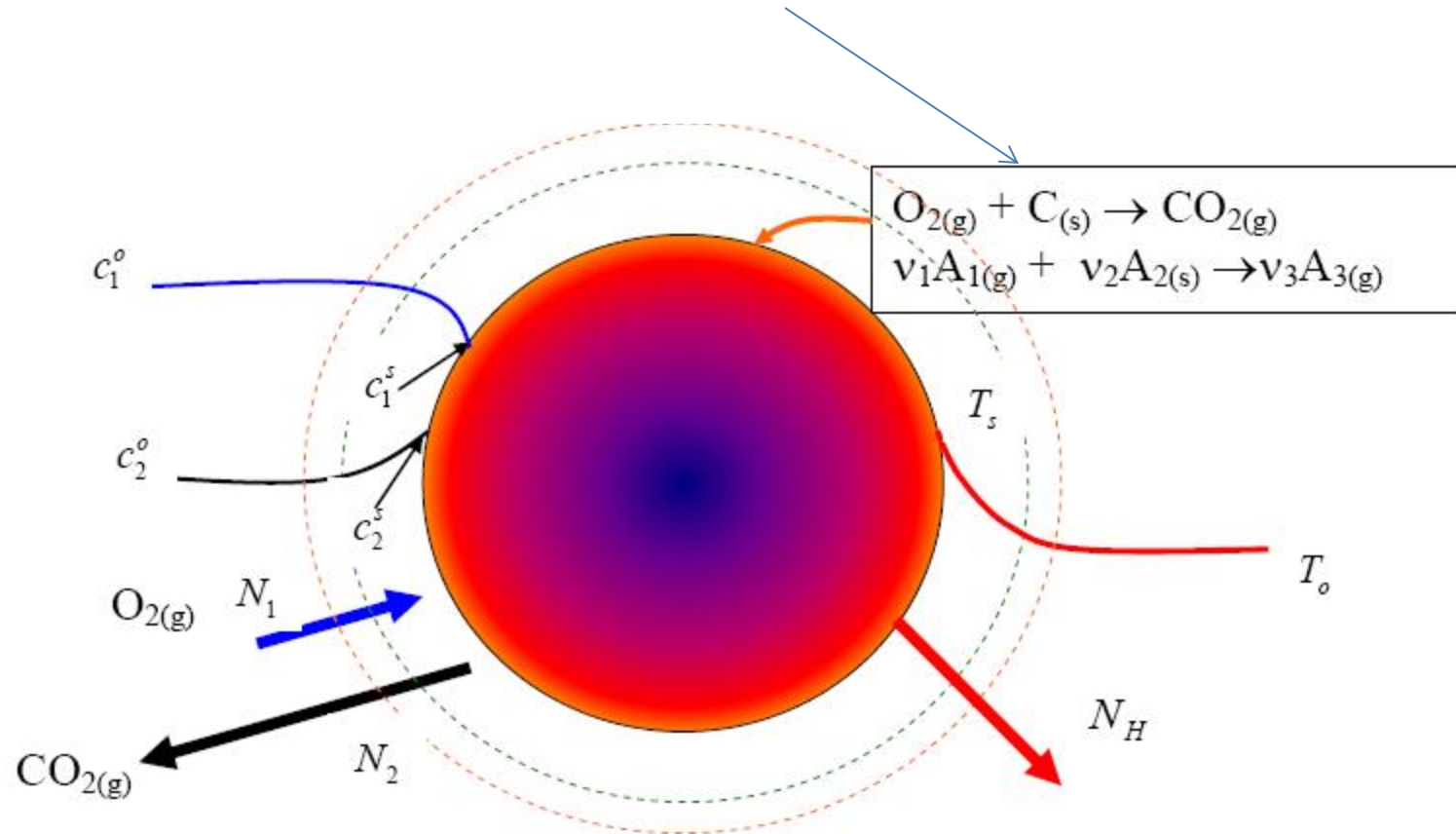
$$\frac{1}{k} \gg \frac{\delta}{D_{O_2}^s}, \frac{1}{k} \gg \frac{1}{k_{cO_2}} \Rightarrow r_s = k c_o, \quad \delta = k c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$



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

External heat and mass transfer

Combustion of the spherical carbon particle



Oxygen molar flux at steady state

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

Energy flux at steady state

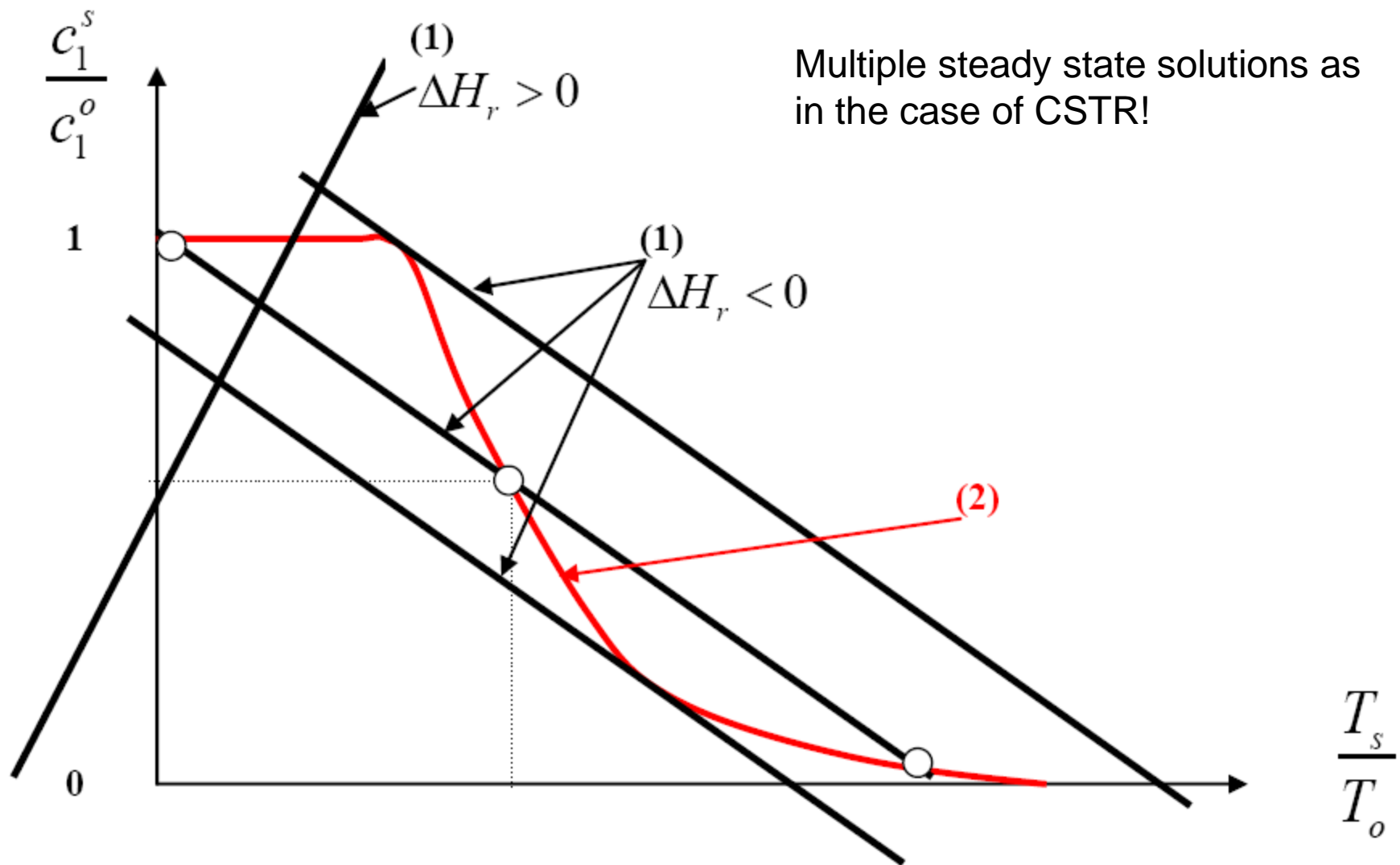
$$N_H = ha(T_s - T_o) = (-\Delta H_r)r_V$$

Surface temperature and concentration of oxygen

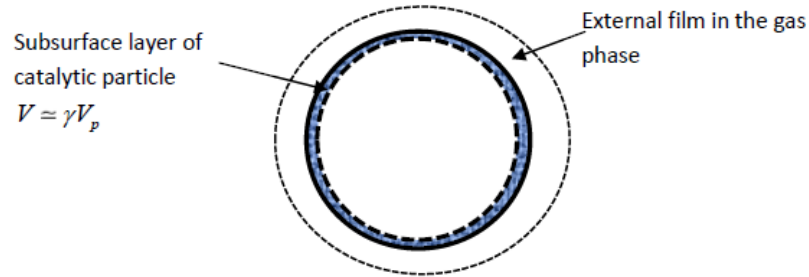
Two balance equations for unknown c_1^s, T_s

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

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



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

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

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



$r_{M,1} = A_1 \exp\left(-\frac{E_1}{RT}\right) P_{s,NH_3} P_{s,O_2} \text{ mol.kg}^{-1}.\text{s}^{-1}$	$A_1 = 4.609 \times 10^{+3} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_1 = 149.1 \text{ kJ.mol}^{-1}$	(1)
$r_{M,2} = A_2 \exp\left(-\frac{E_2}{RT}\right) P_{s,NH_3} P_{s,O_2} \text{ mol.kg}^{-1}.\text{s}^{-1}$	$A_2 = 5.0 \times 10^{-2} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_2 = 61.0 \text{ kJ.mol}^{-1}$	(2)
$r_{M,3} = A_3 \exp\left(-\frac{E_3}{RT}\right) P_{s,NH_3} P_{s,O_2} \text{ mol.kg}^{-1}.\text{s}^{-1}$	$A_1 = 2.8 \times 10^{-2} \text{ mol.kg}^{-1}.\text{s}^{-1}.\text{Pa}^{-2}$ $E_1 = 104.0 \text{ kJ.mol}^{-1}$	(3)

Catalytic reactions

• homogeneous catalysis

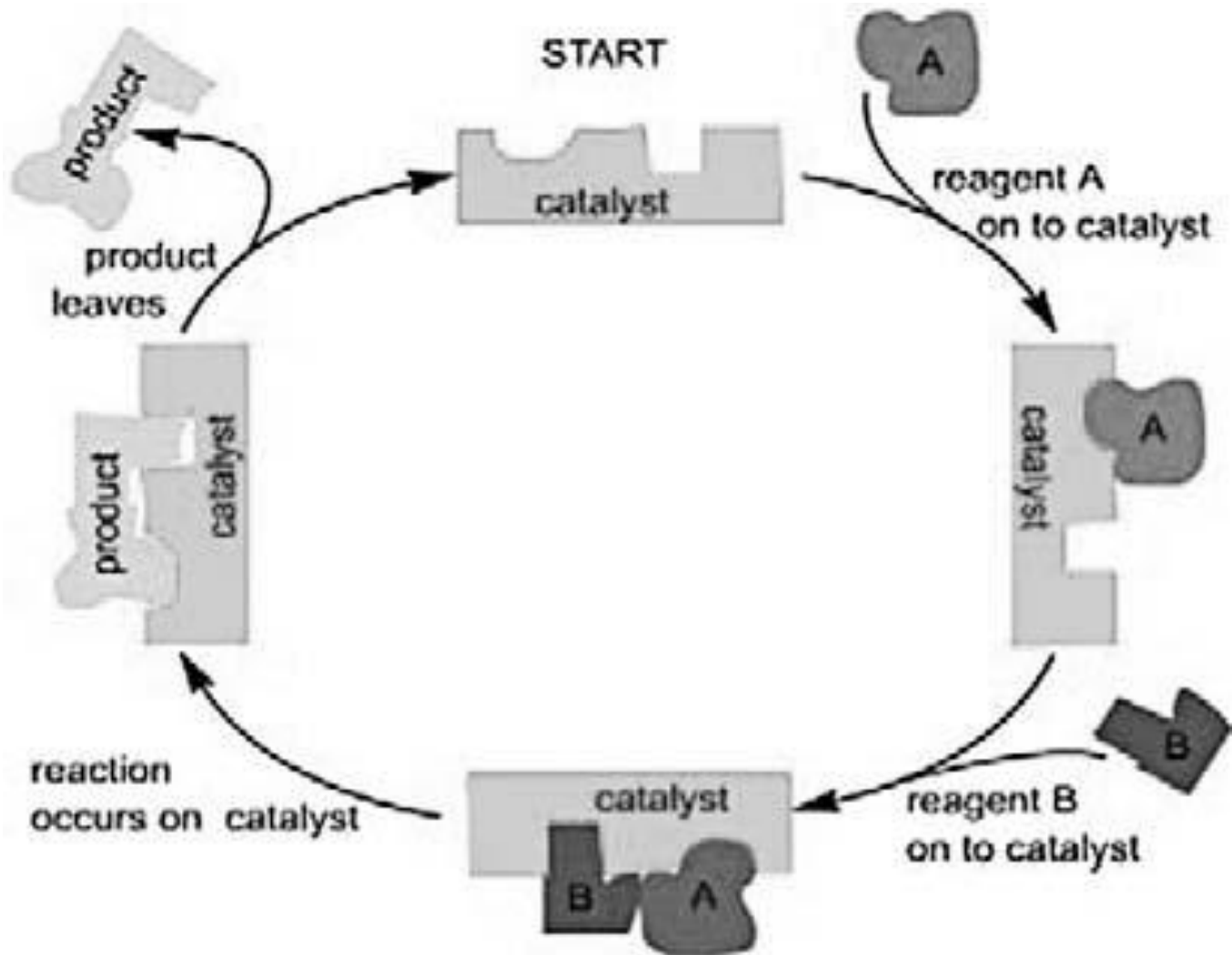
- Ozone decomposition in the presence of Cl
- SO₂ oxidation by NO_x
- Esterification catalyzed by acids or bases
- Enzymatic catalysis



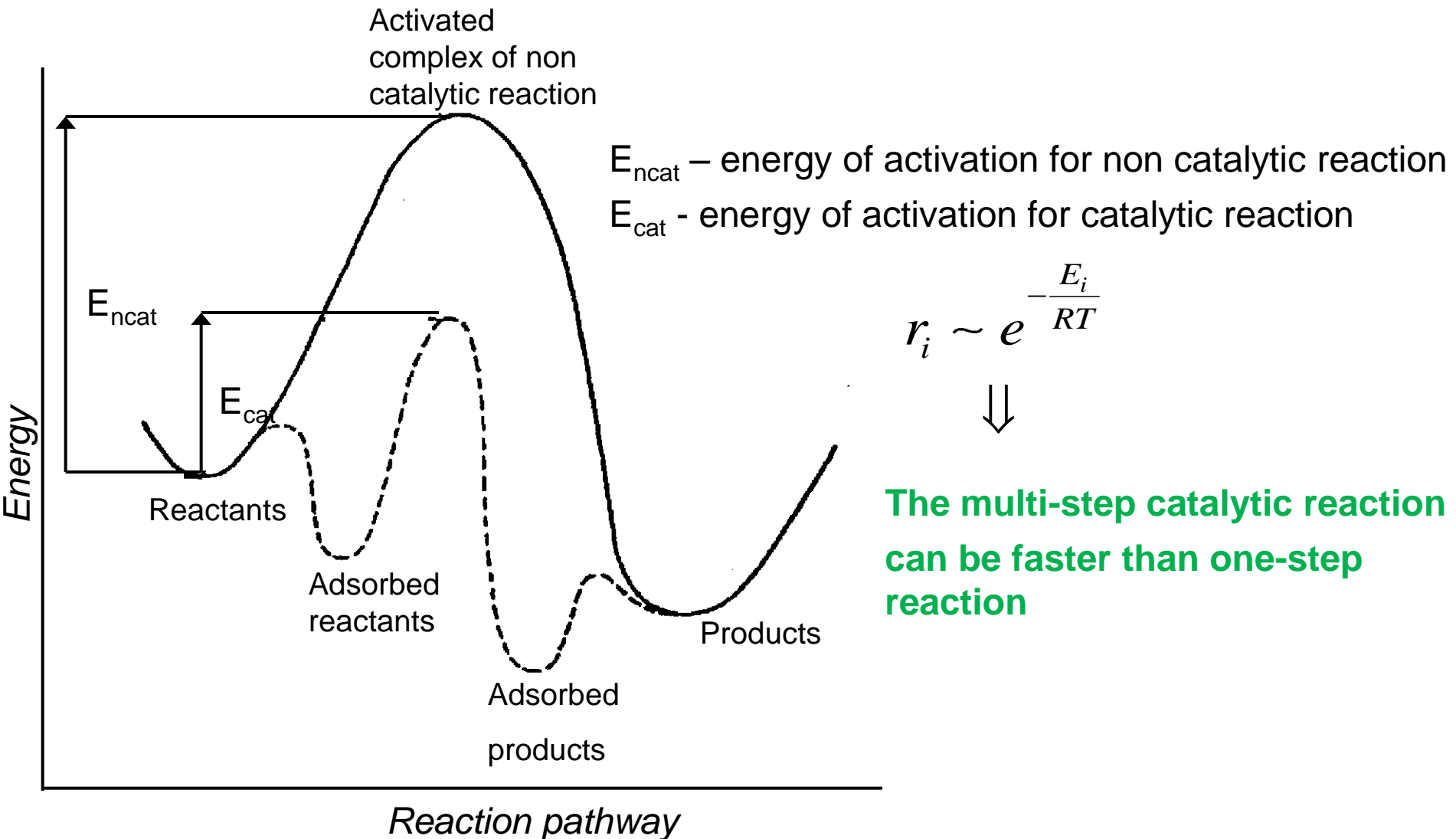
• heterogeneous catalysis

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

Catalytic cycle



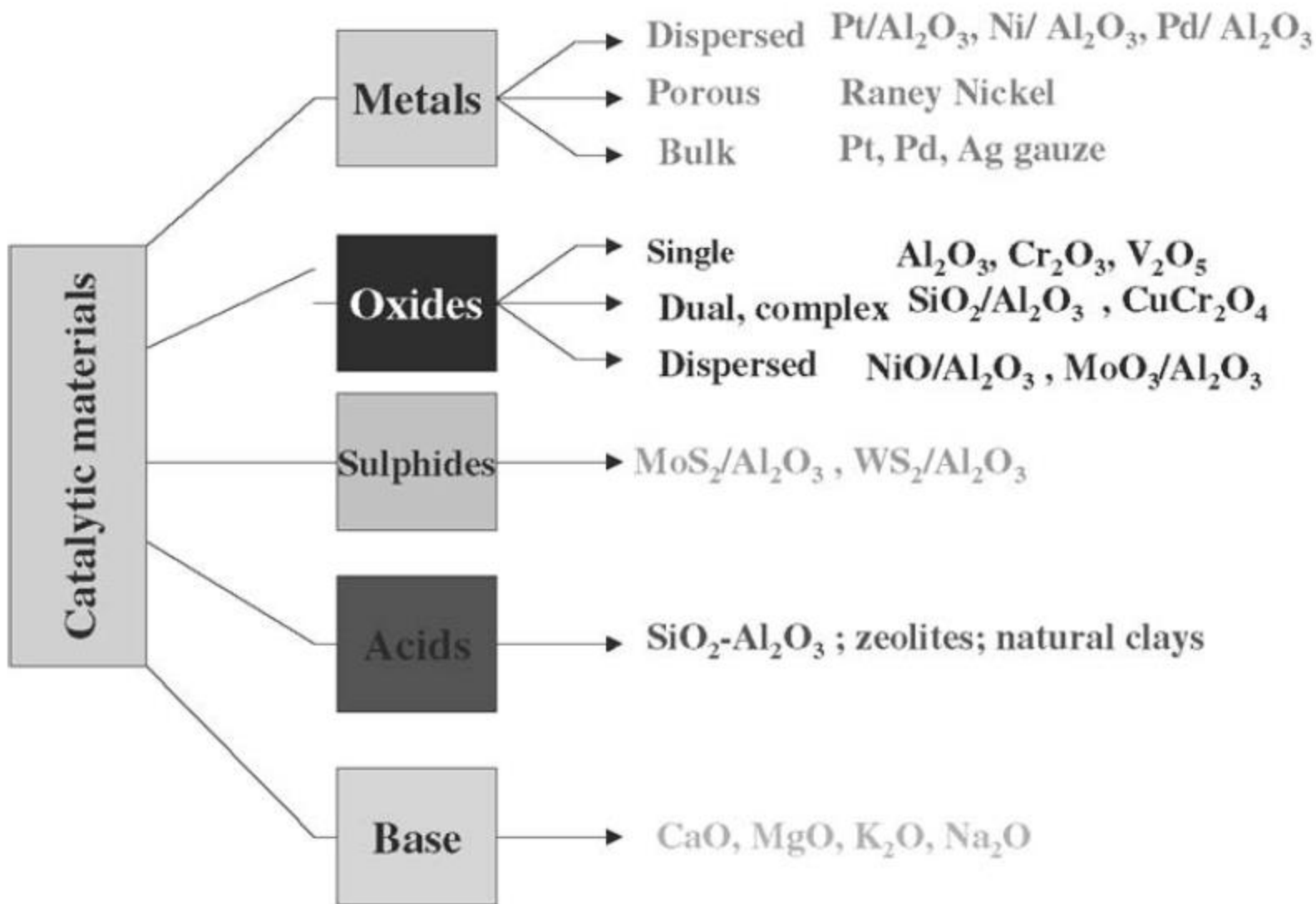
Non catalytic x catalytic reaction



Homogeneous x Heterogeneous Catalysts

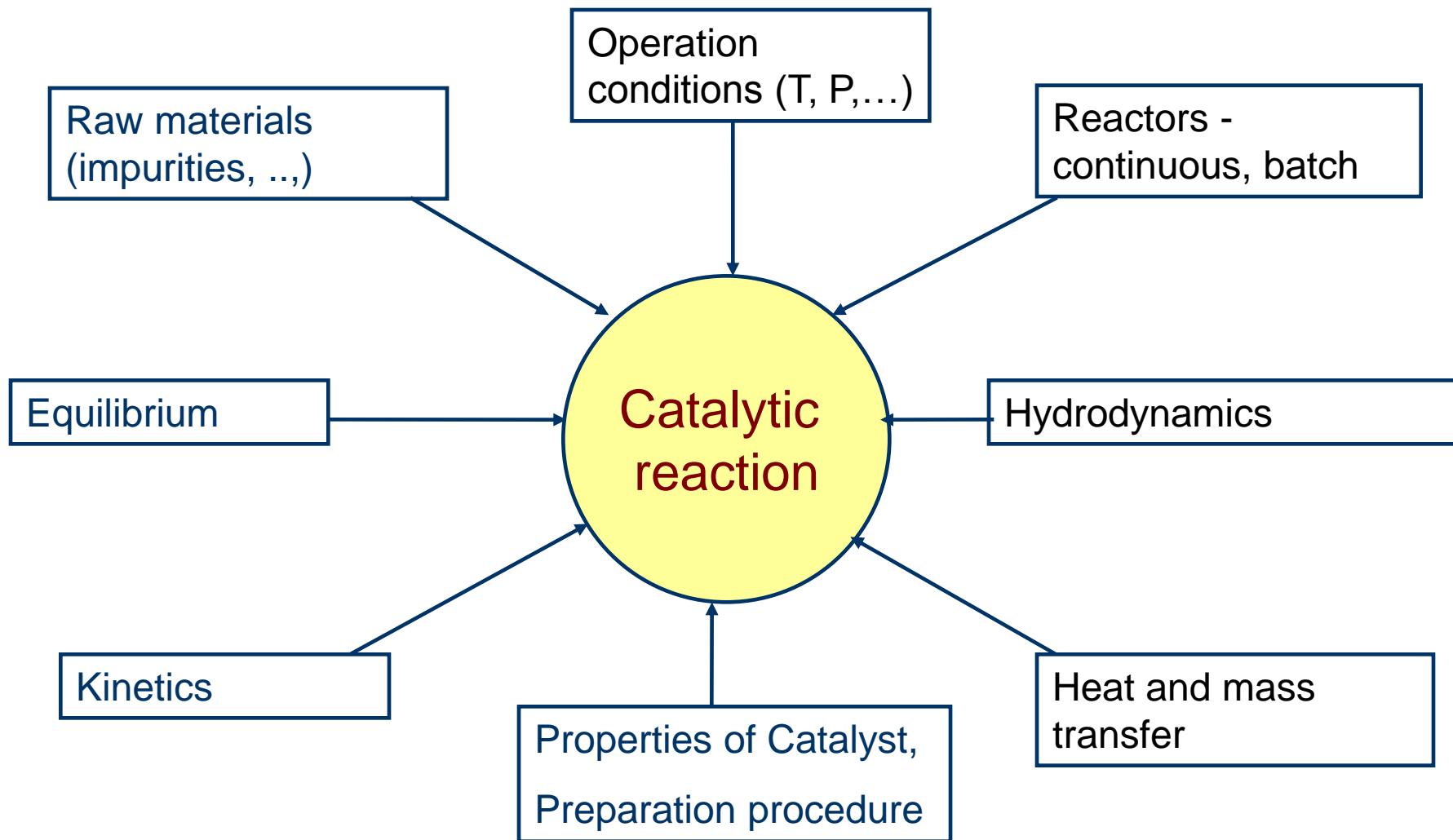
		Homogeneous	Heterogeneous
Active sites	Concentration	All atoms	Surface atoms
	Diffusion disguises	Low	High (variable)
	Reaction conditions	No	Important
	Application	50-200 °C	200-1000 °C
		Limited	Large
Characterization	Structure, composition	Well defined	No clear defintion
	Modification	Easy	Difficult
	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	$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$

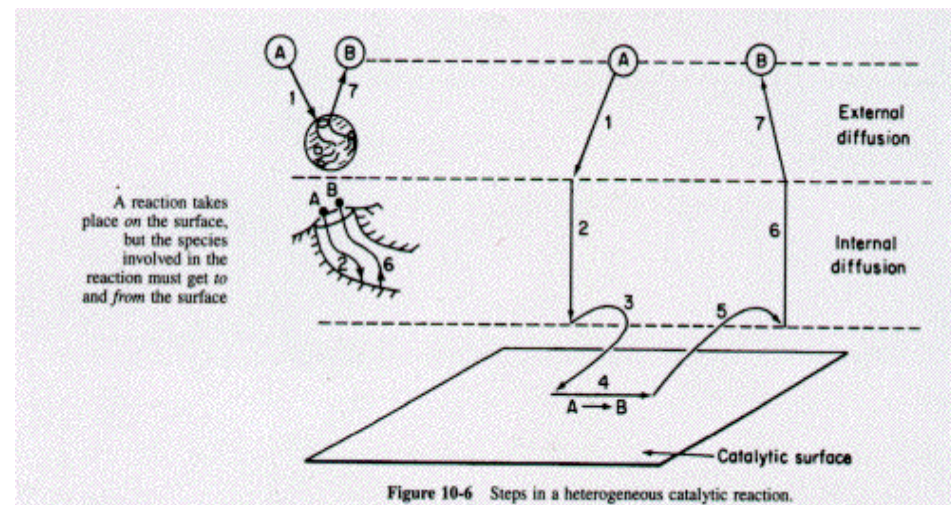


Steps in a catalytic reaction

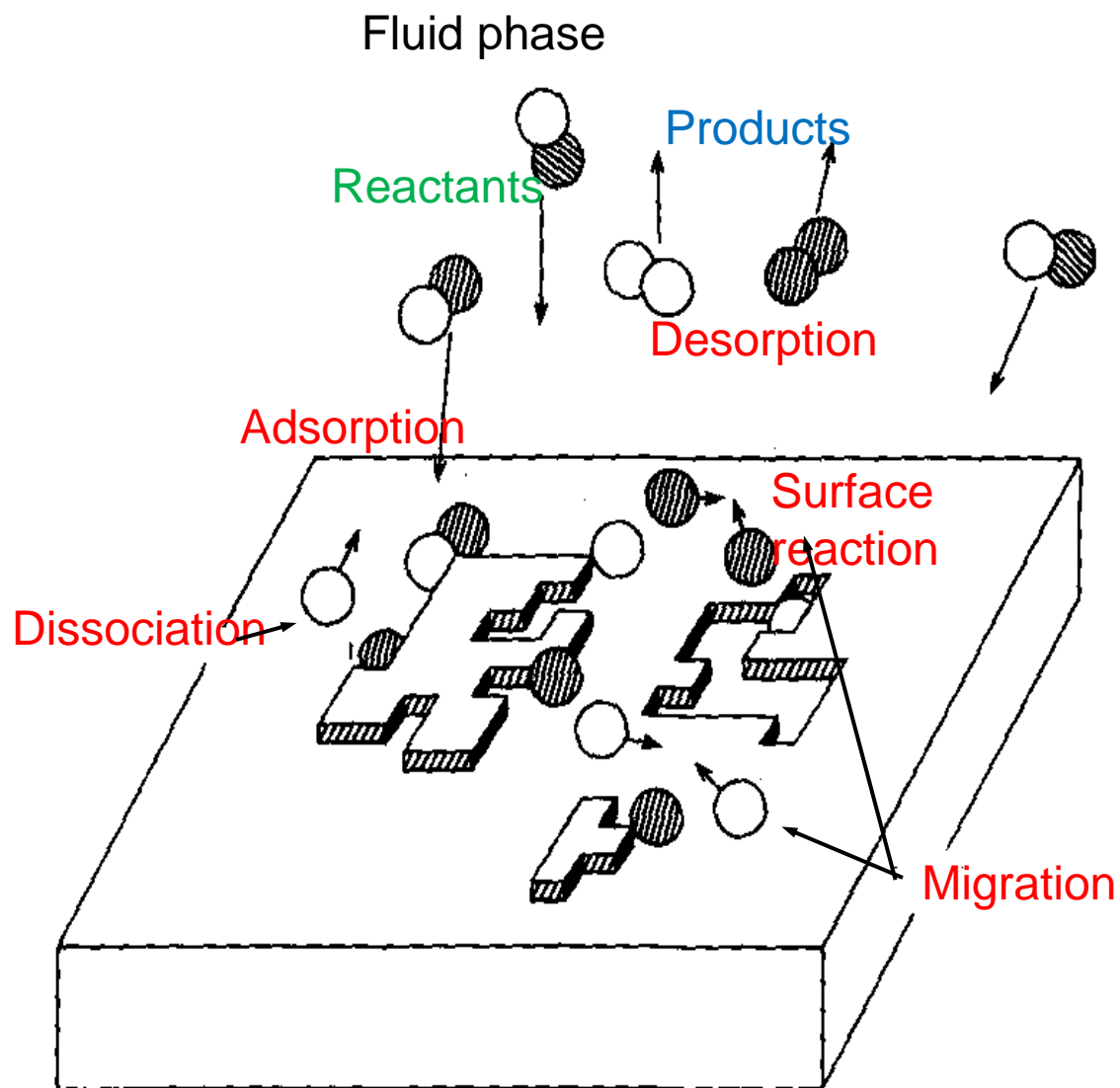
- 1) Mass transfer of reactants to the external surface of catalyst
- 2) Mass transfer of reactants in porous structure of catalyst
- 3) *Adsorption of reactants*
- 4) *Surface reaction (+ migration)*
- 5) *Desorption of products*
- 6) Mass transfer of products in porous structure of catalyst
- 7) Mass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



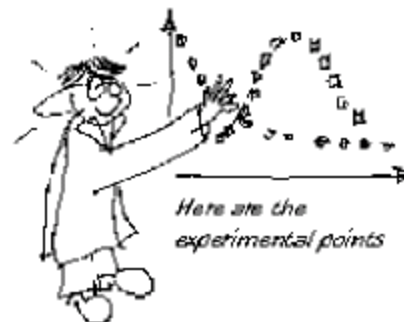
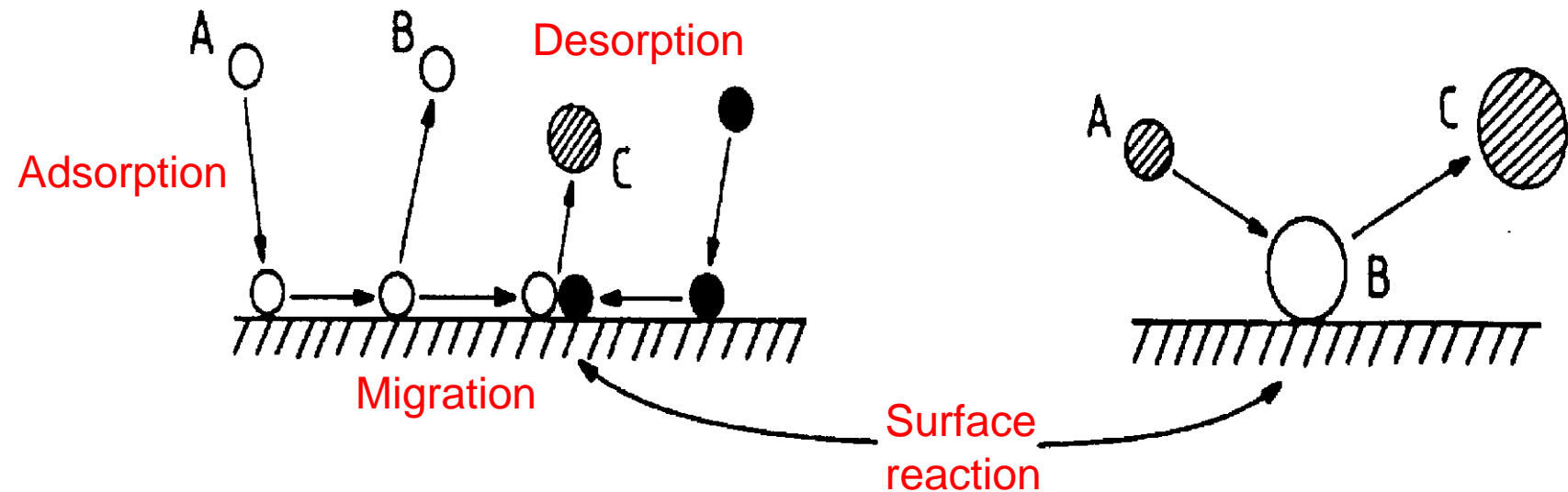
Elementary steps of catalytic reaction



Mechanisms in heterogeneous catalysis

Langmuir-Hinshelwood

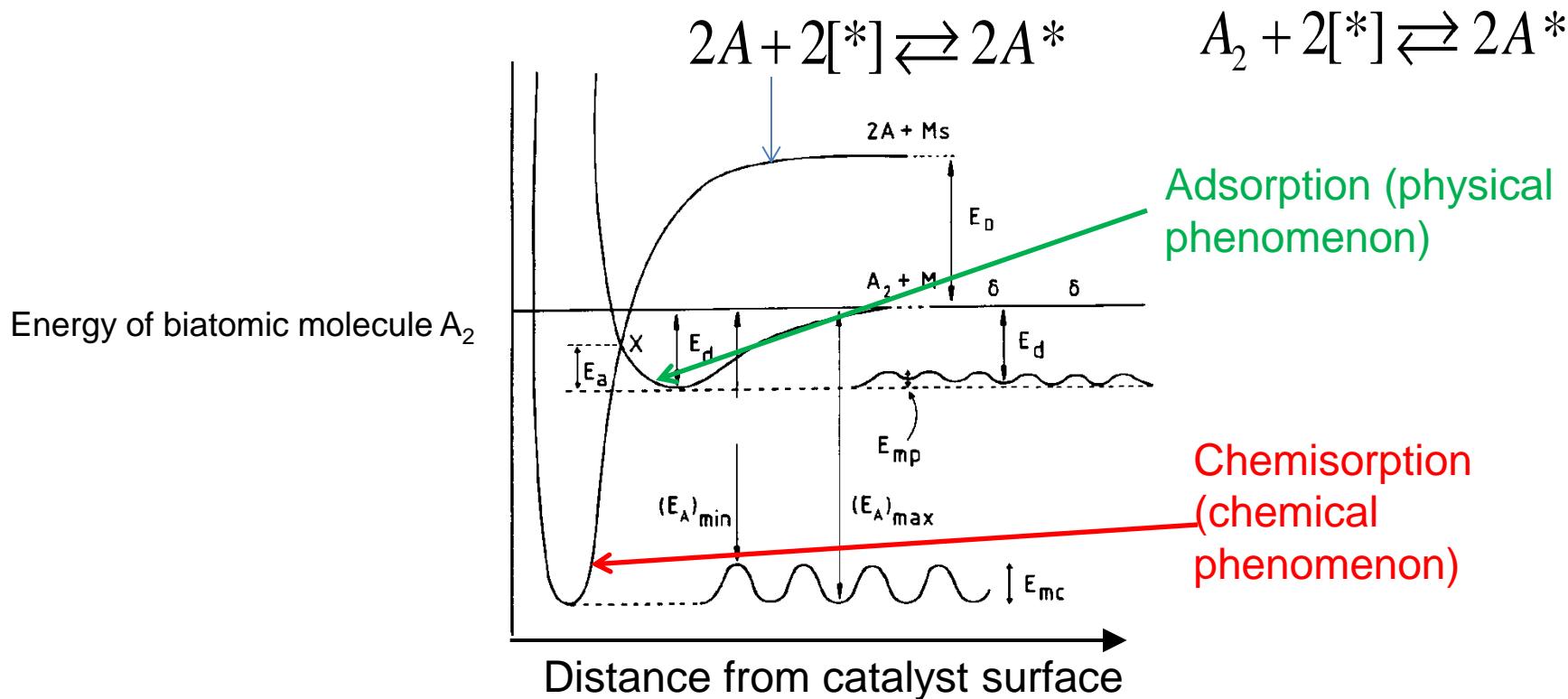
Rideal-Eley



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

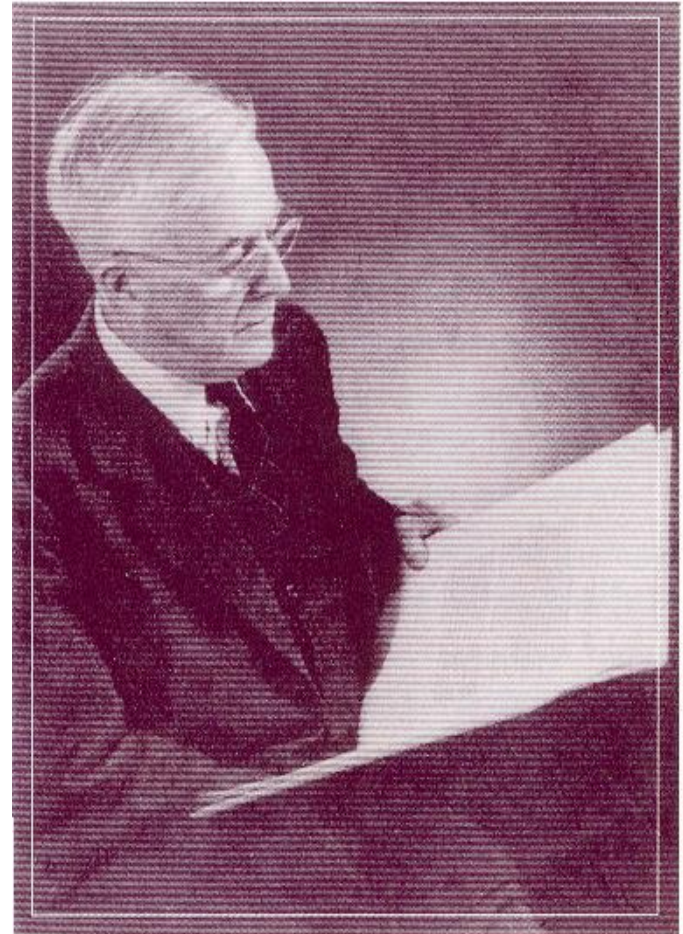
Adsorption (chemisorption) isotherm – Surface occupancy as a function of partial pressure of given component at constant temperature

Henry isotherm

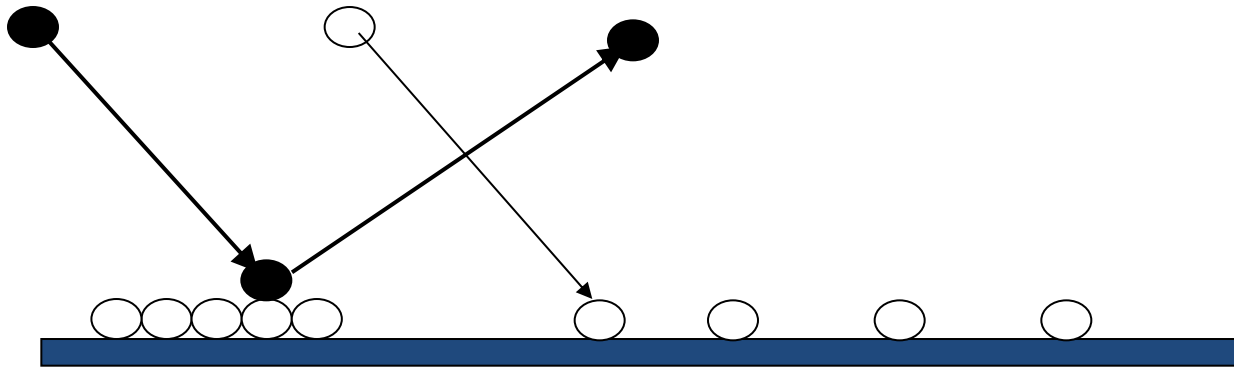
$$\Theta_i = H_i \cdot p_i$$

Irving Langmuir

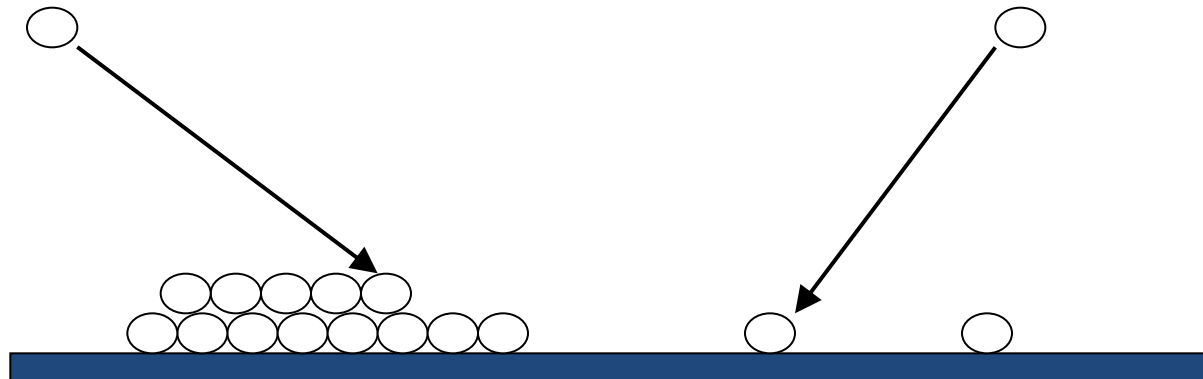
- 1920 - adsorption isotherm
- kinetics of catalytic reactions on ideal surfaces
- 1932 - Nobel Prize



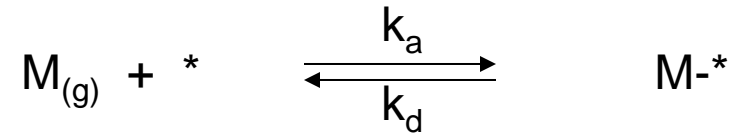
Langmuir adsorption isotherm



Brunauer-Emmett-Teller (BET) adsorption isotherm



Associative adsorption



* - active site, k_a and k_d – kinetic constants for adsorption and desorption

Adsorption rate = $k_a \cdot p \cdot (1 - \Theta)$ p = partial pressure of adsorbate

Desorption rate = $k_d \cdot \Theta$

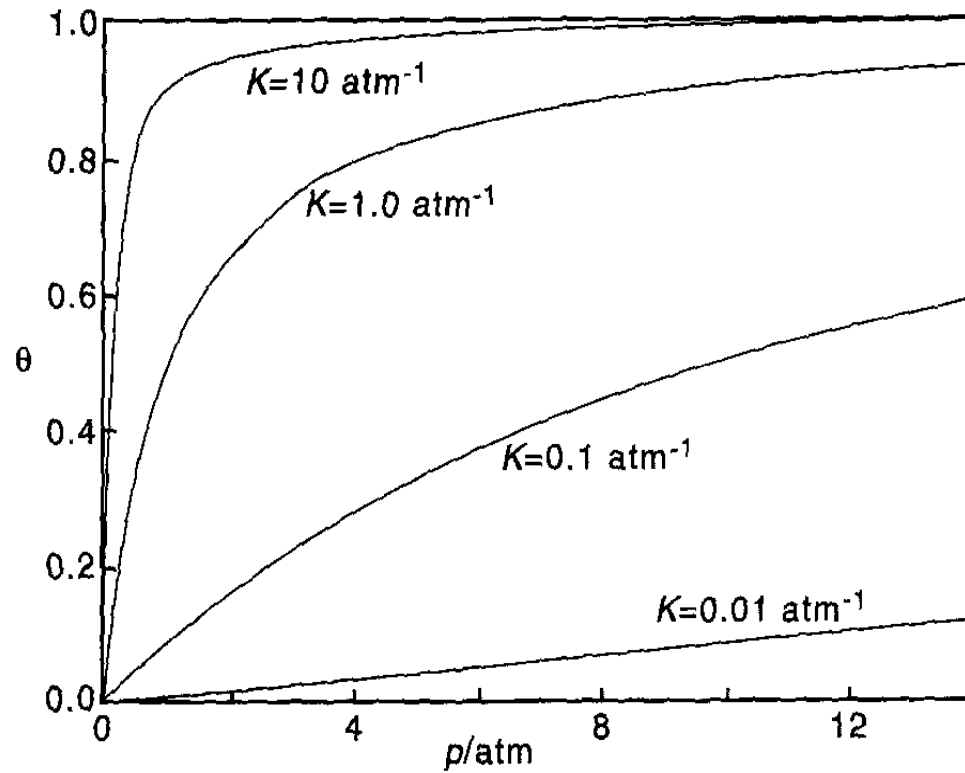
Equilibrium

$$k_a \cdot p \cdot (1 - \Theta) = k_d \cdot \Theta$$

Langmuir adsorption isotherm

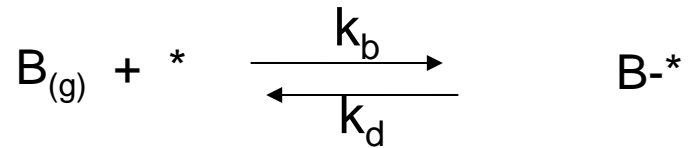
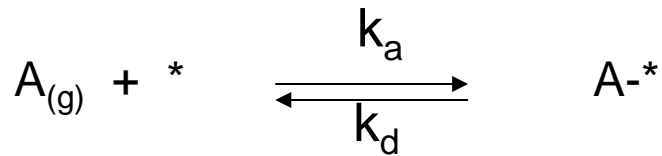
$$\Theta = N_s / N = K \cdot p / (1 + K \cdot p) \quad (K = k_a / k_d)$$

Associative chemisorption



Langmuir adsorption (chemisorption) isotherm

Multicomponent associative chemisorption



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

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

$$K_A = k_a / k_d$$

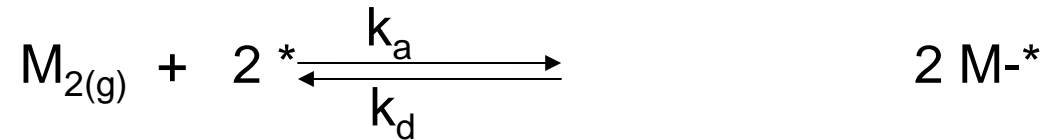
$$K_B = k_b / k_d$$

Irreversible chemisorption



catalyst poisoning

Dissociative chemisorption



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

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

$$k_a \cdot p \cdot (1 - \Theta)^2 = k_d \cdot \Theta^2 \quad (K' = k_a/k_d)$$

$$\frac{\Theta^2}{(1 - \Theta)^2} = K' \cdot p \quad \Rightarrow \quad \Theta = \frac{\sqrt{K' \cdot p}}{1 + \sqrt{K' \cdot p}}$$

Isotherms

Langmuir

(chemisorption, adsorption, monolayer, micropores)

$$\frac{n_{ads}}{n_*} = \Theta = \frac{K \cdot p}{1 + K \cdot p}$$

Henry

(chemisorption, adsorption, low occupancy)

$$\frac{n_{ads}}{n_*} = \Theta = H p$$

Freundlich

(chemisorption, adsorption, non ideal)

$$\frac{n_{ads}}{n_*} = \Theta = K p^{\frac{1}{n}}$$

Temkin

(chemisorption, non ideal)

$$\Theta = A \ln[B p]$$

Brunauer-Emmett-Teller (BET)

(adsorption, multilayer)

$$\frac{p}{n_{ads}(p_0 - p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C p_0}$$

Virial

(adsorption, multilayer)

$$\frac{p}{R \cdot T} = \Theta(1 + a_1 \Theta + a_2 \Theta^2 + \dots)$$

Brunauer-Emmett-Teller (BET)

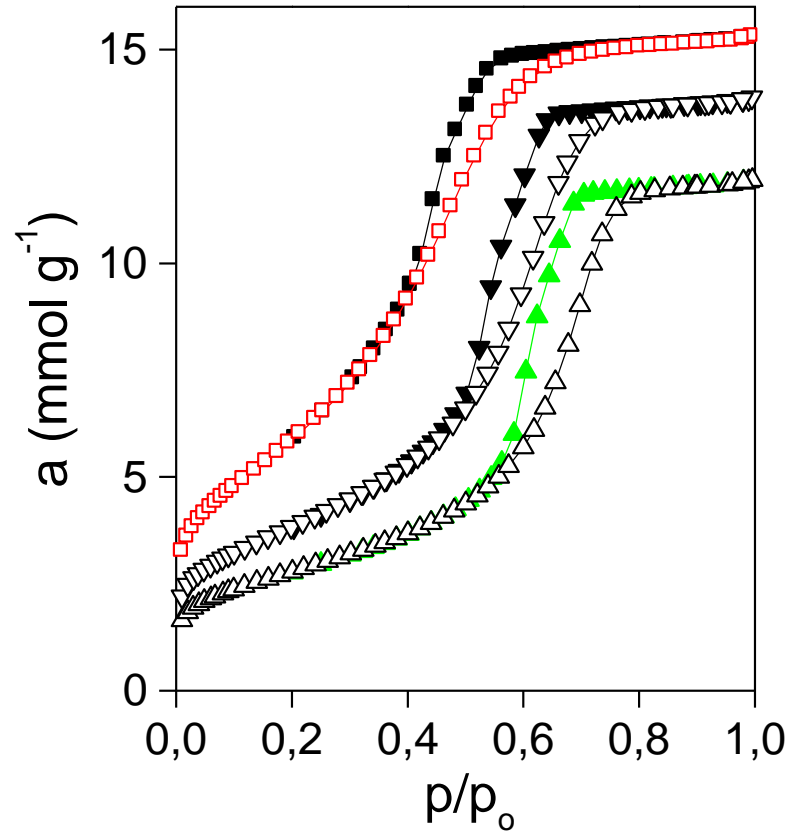
Extention of Langmuir model

Assumptions:

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

$$\frac{p}{n_{ads}(p_0 - p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C p_0}$$

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

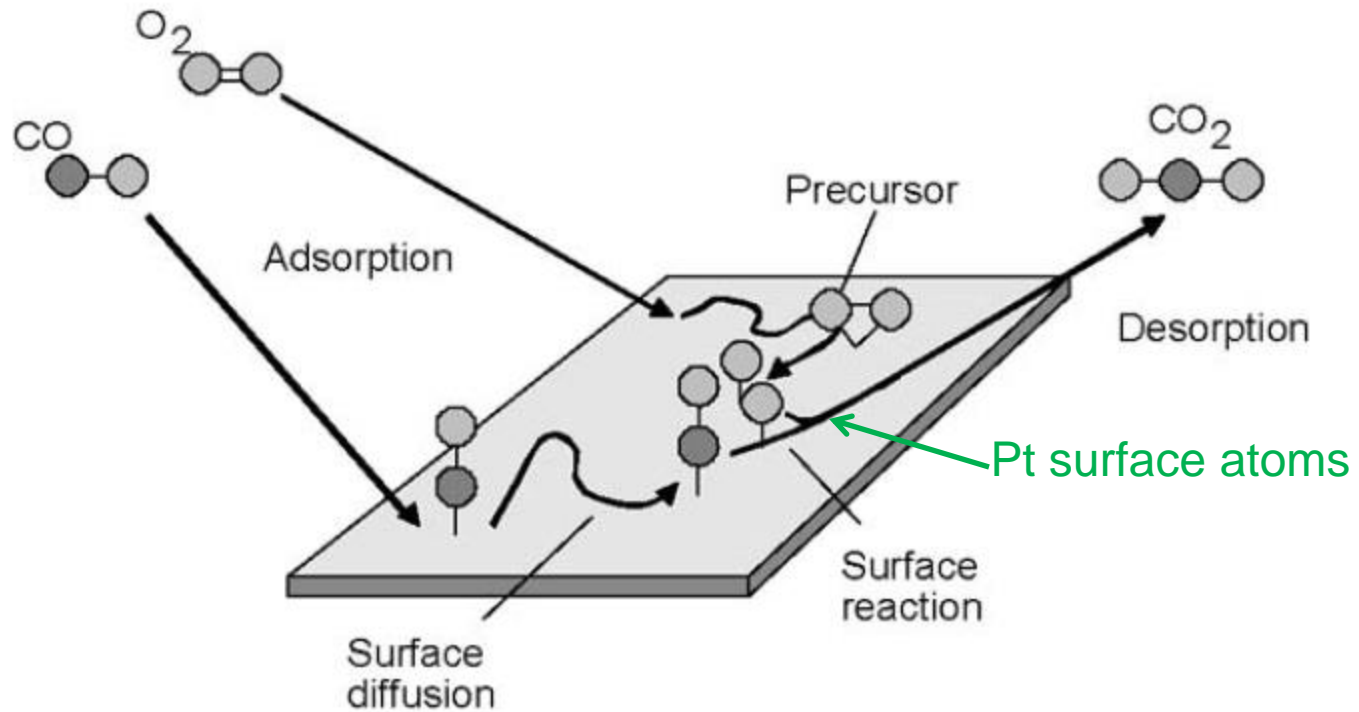
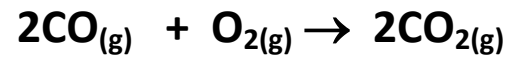
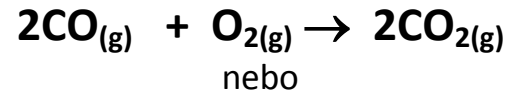
Langmuir-Hishelwood ideal surface

⊙ Rate of elementary steps

⊙ Rate determining step x steady state hypothesis

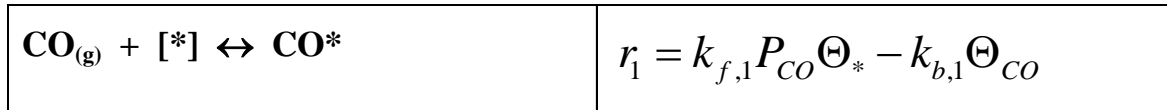
CO oxidation on Pt

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



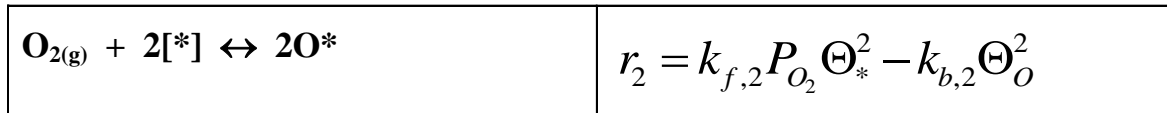
Elementary steps of catalytic CO oxidation on Pt

1. CO chemisorption

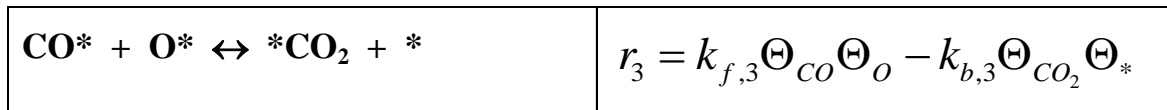


2. O₂ dissociative chemisorption

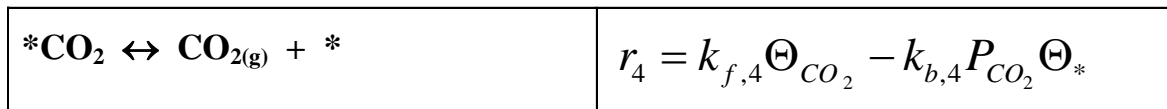
* - Pt surface atoms = Catalytic active centre



3. Surface reaction between CO* and O*



4. CO₂ desorption into gas phase



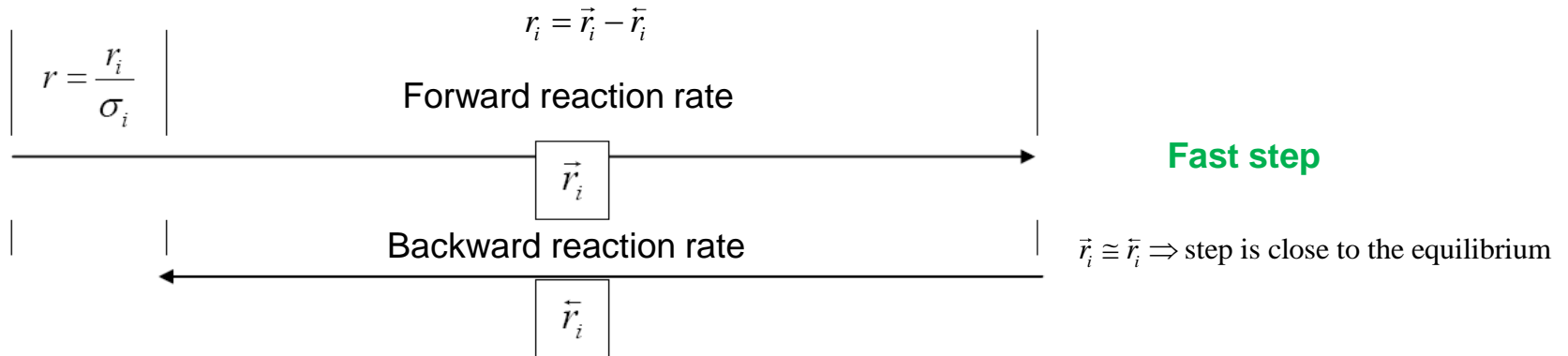
P_i – partial pressures of gaseous components [Pa]

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



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

Rate determining step: surface reaction

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

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

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

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

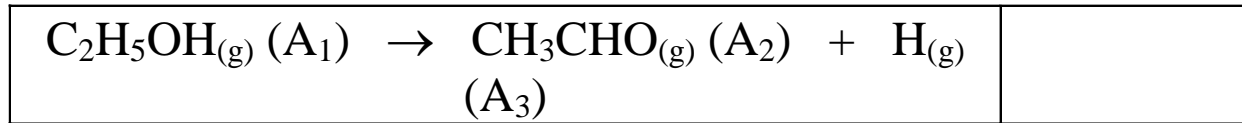
$$\Theta_O = \frac{\sqrt{K_{O_2} P_{O_2}}}{1 + K_{CO} P_{CO} + \sqrt{K_{O_2} P_{O_2}} + K_{CO_2} P_{CO_2}}$$

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

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

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

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

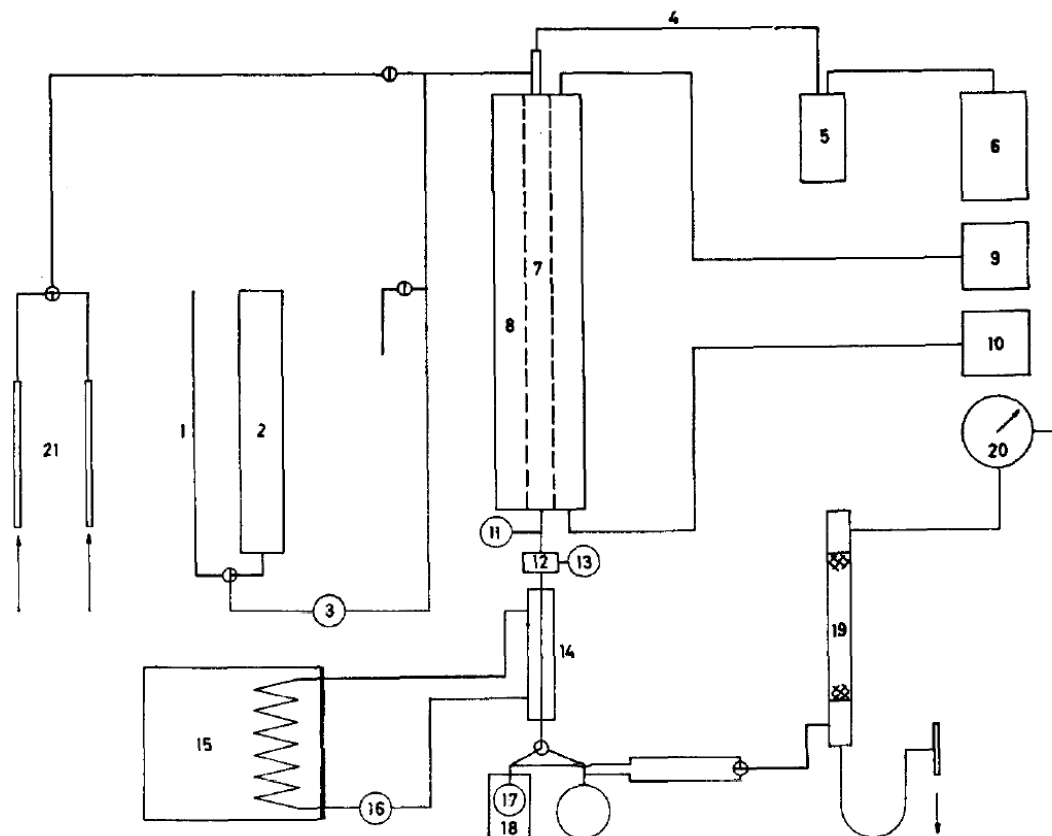


FIG. 1. Apparatus: 1,2, feed burettes; 3, metering pump; 4, thermocouples; 5, ice-bath; 6, mV-recorder; 7, reactor; 8, reactor-mantle; 9,10, variable transformers; 11,13, manometers; 12, pressure regulating device; 14, cooler; 15, cooling unit; 16, circulating pump; 17, sampling flask; 18, liquid air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

Prklad_9_1.awv - Athena Visual Studio

File Edit Model Build View Format Tools VisualKinetics Windows Help

Prklad_9_1.awv

```
! 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

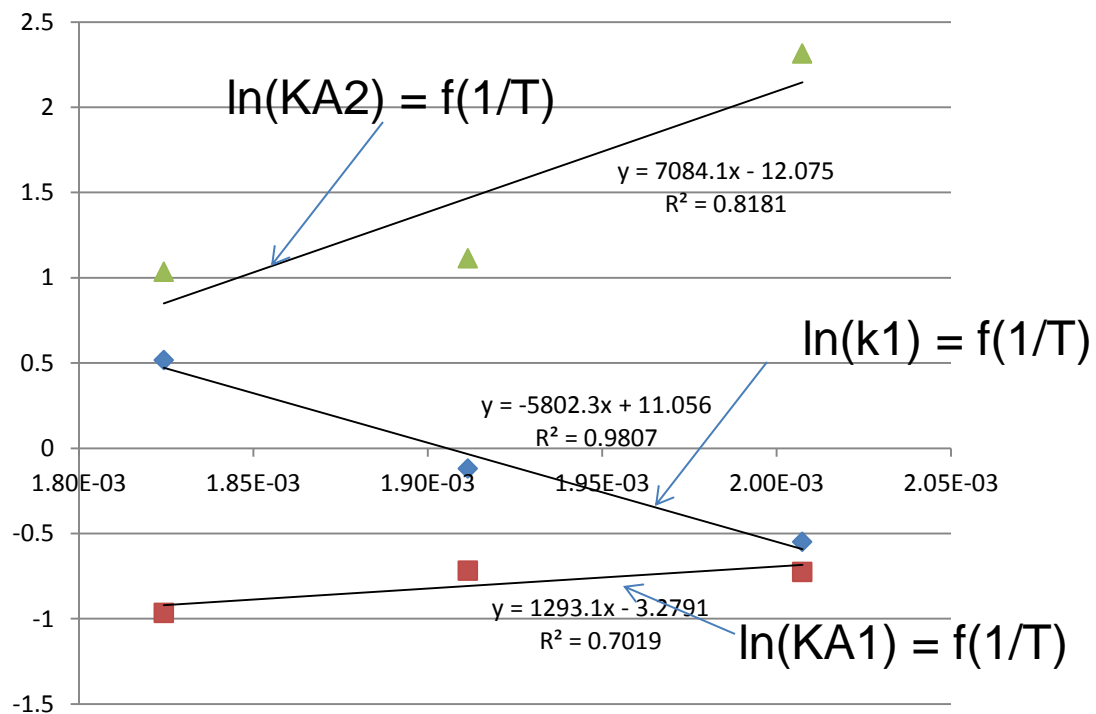
@Initial Conditions
U(1)=0.0

@Model Equations
Dir PA1, PA2, PA3, PA4, KEQ, X1, RR, AUX As Real
KEQ = DEXF (-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)
```

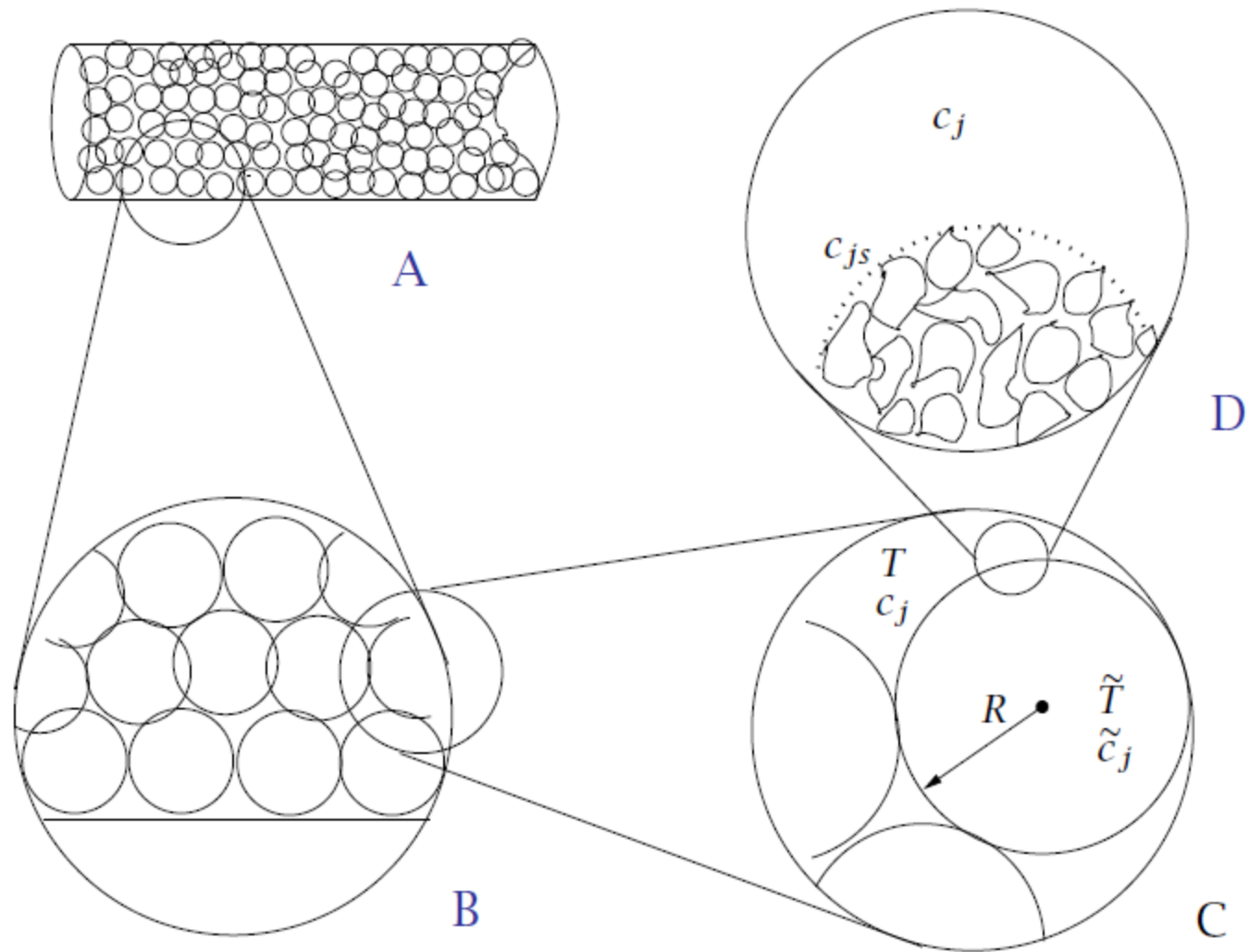
Compiler Selected: Intel Visual Fortran Dec-08-2009 10:55:19 INS Ln 1/36 Col 1 ©Athena Visual Software, Inc.

	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



Models of 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.

Single Reaction in an Isothermal Particle

- We start with the simplest cases and steadily remove restrictions and increase the generality. We consider in this section a single reaction taking place in an *isothermal* particle.
- First case: the spherical particle, first-order reaction, without external mass-transfer resistance.

First-Order Reaction in a Spherical Particle



$$0 = D_j \nabla^2 c_j + R_j, \quad j = 1, 2, \dots, n_s$$

Substituting the production rate into the mass balance, expressing the equation in spherical coordinates, and assuming pellet symmetry in θ and ϕ coordinates gives

$$D_A \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dc_A}{dr} \right) - kc_A = 0$$

in which D_A is the effective diffusivity in the pellet for species A.

As written here, the first-order rate constant k has units of inverse time.

Be aware that the units for a heterogeneous reaction rate constant are sometimes expressed per mass or per area of catalyst.

Boundary Conditions

- We require *two* boundary conditions for Equation
- In this section we assume the concentration at the outer boundary of the pellet, c_{As} , is known
- The symmetry of the spherical pellet implies the vanishing of the derivative at the center of the pellet.
- Therefore the two boundary conditions for Equation are

$$\begin{aligned} c_A &= c_{As}, & r &= R \\ \frac{dc_A}{dr} &= 0 & r &= 0 \end{aligned}$$

Dimensionless form

At this point we can obtain better insight by converting the problem into dimensionless form. Equation has two dimensional quantities, length and concentration. We might naturally choose the sphere radius R as the length scale, but we will find that a better choice is to use the pellet's volume-to-surface ratio. For the sphere, this characteristic length is

$$a = \frac{V_p}{S_p} = \frac{\frac{4}{3}\pi R^3}{4\pi R^2} = \frac{R}{3}$$

The only concentration appearing in the problem is the surface concentration in the boundary condition, so we use that quantity to nondimensionalize the concentration

$$\bar{r} = \frac{r}{a}, \quad \bar{c} = \frac{c_A}{c_{As}}$$

Dividing through by the various dimensional quantities produces

$$\frac{1}{\bar{r}^2} \frac{d}{d\bar{r}} \left(\bar{r}^2 \frac{d\bar{c}}{d\bar{r}} \right) - \Phi^2 \bar{c} = 0$$

$$\bar{c} = 1 \quad \bar{r} = 3$$

$$\frac{d\bar{c}}{d\bar{r}} = 0 \quad \bar{r} = 0$$

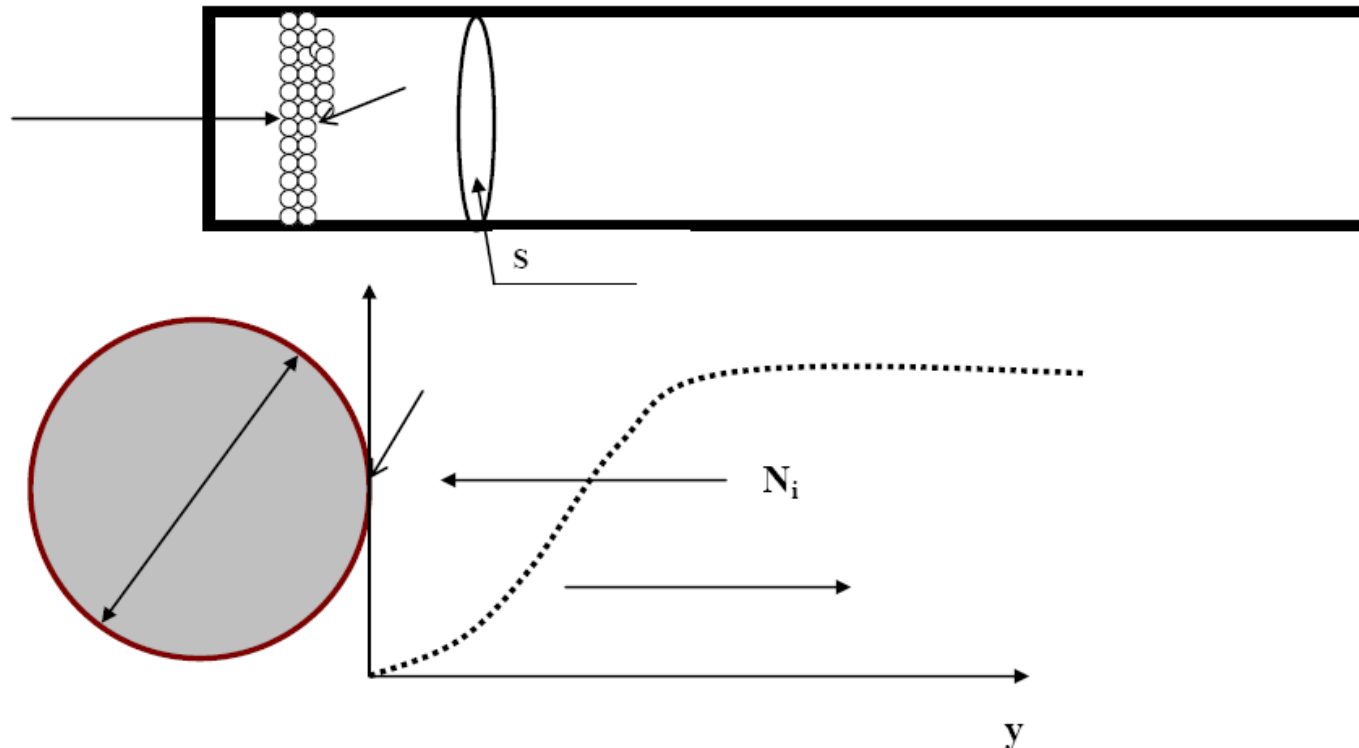
in which Φ is given by

$\Phi = \sqrt{\frac{ka^2}{D_A}}$	$\frac{\text{reaction rate}}{\text{diffusion rate}}$	Thiele modulus
----------------------------------	--	----------------

Models of catalytic reactors

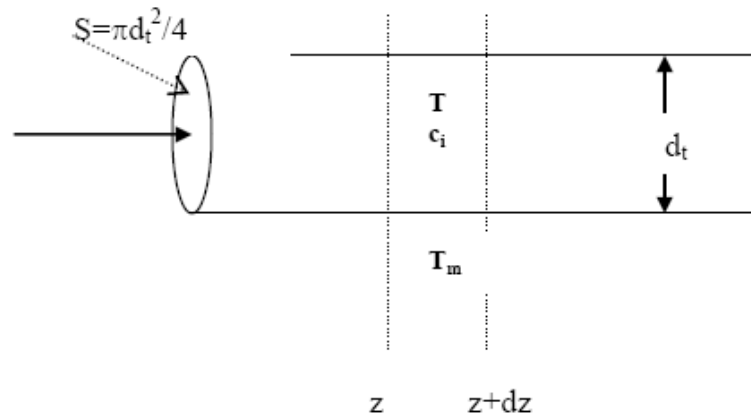
Model equations involve:

- 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	<ul style="list-style-type: none"> • 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



$$\frac{dF_i}{dz} = S \nu_i r_V$$

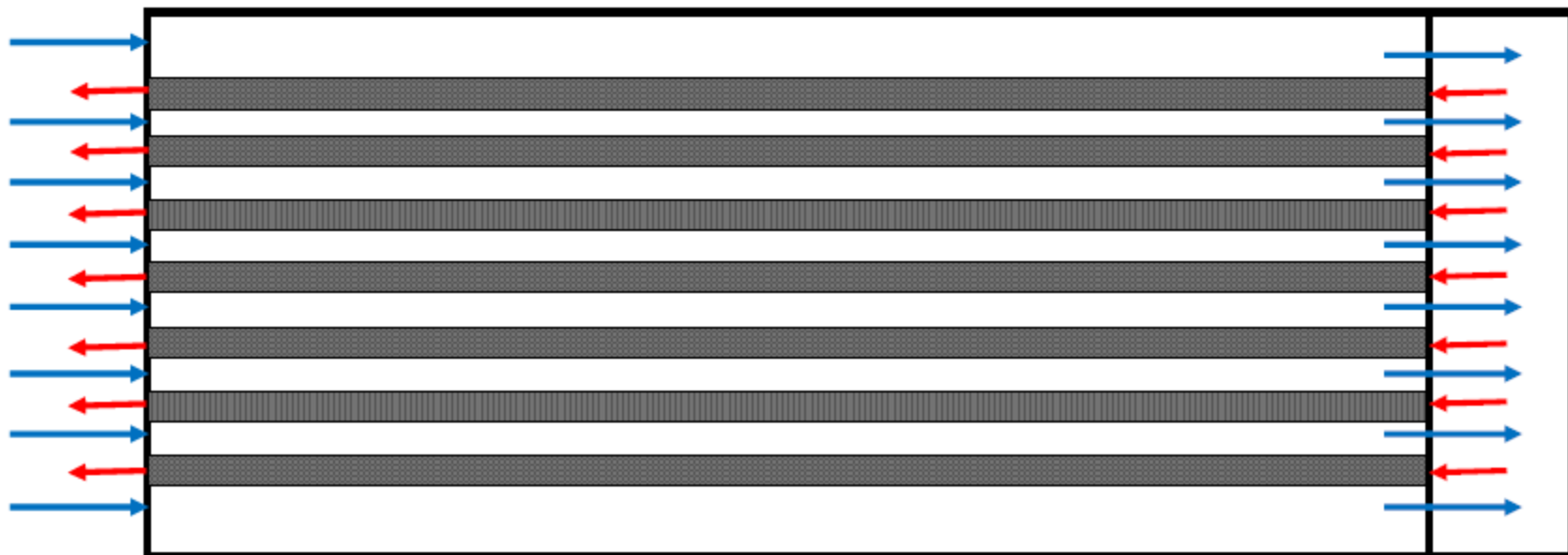
$$\dot{m} \bar{c}_p \frac{dT}{dz} = (-\Delta H_r) S r_V + \frac{\pi d_t}{\pi d_t^2 / 4} K (T_m - T) = (-\Delta H_r) S r_V + \frac{4}{d_t} K (T_m - T)$$

$$-\frac{dP}{dz} = f \frac{\rho_g u_s^2}{d_p}$$

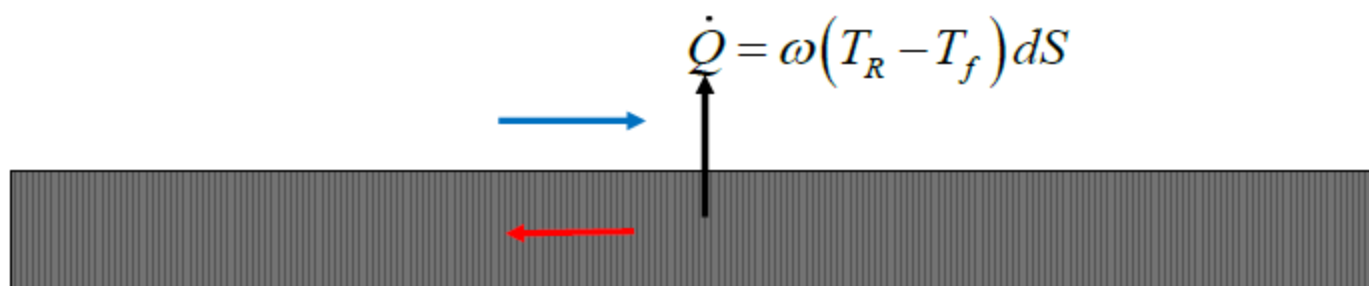
$$z = 0$$

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

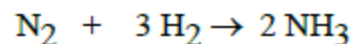
d_p	effective diameter of catalytic particle
f	friction coefficient
u_s	mean fluid velocity
K	overall heat transfer coefficient



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.



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



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

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

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

$$R = 8.31446 \text{ J/mol/K}$$

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

$$z = 0 \quad -\varepsilon D_{ai} \frac{dc_i}{dz} + c_i v_z = c_i^o v_z \quad -\lambda_{am} \frac{dT}{dz} + v_z \rho_g c_{pm} T = v_z \rho_g c_{pm} T_o$$

$$z = L \quad \frac{dc_i}{dz} = 0 \quad \frac{dT}{dz} = 0$$

Dimensionless form

$$x = \frac{z}{L} \quad Y_i = \frac{c_i}{c_i^o} \quad \vartheta = \frac{T}{T_o}$$

$$\frac{1}{Pe_{Mi}} \frac{d^2 Y_i}{dx^2} - \frac{dY_i}{dx} + Da_i R(Y_k, \vartheta) = 0$$

$$\frac{1}{Pe_H} \frac{d^2 \vartheta}{dx^2} - \frac{d\vartheta}{dx} + \beta R(Y_k, \vartheta) = 0$$

$$x = 0 \quad \frac{1}{Pe_{Mi}} \frac{dY_i}{dx} = Y_i - 1 \quad \frac{1}{Pe_H} \frac{d\vartheta}{dx} = \vartheta - 1$$

$$x = 1 \quad \frac{dY_i}{dx} = 0 \quad \frac{d\vartheta}{dx} = 0$$

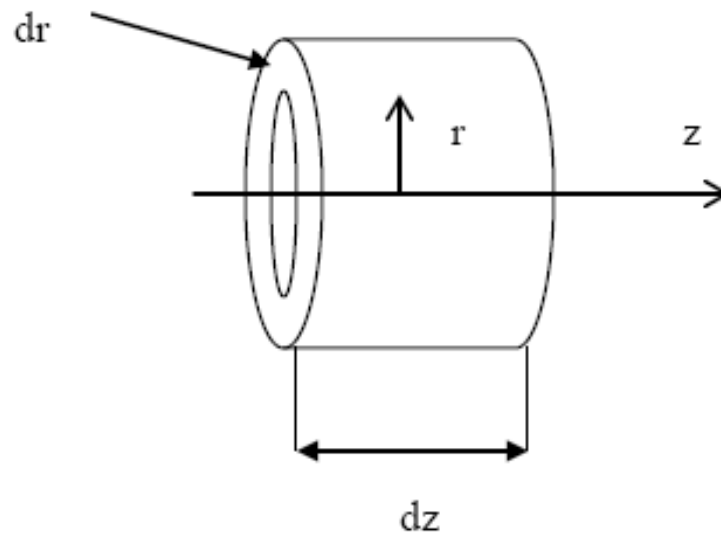
$$Pe_{Mi} = \frac{v_z L}{\varepsilon D_{ai}} \quad Pe_H = \frac{v_z L}{\lambda_{am}} \quad Da_i = \frac{L r_V(c_k^o, T_o)}{c_i^o v_z} \quad \beta = \frac{L r_V(c_k^o, T_o)(-\Delta H_r)}{v_z c_{pm} \rho_g v_z T_o}$$

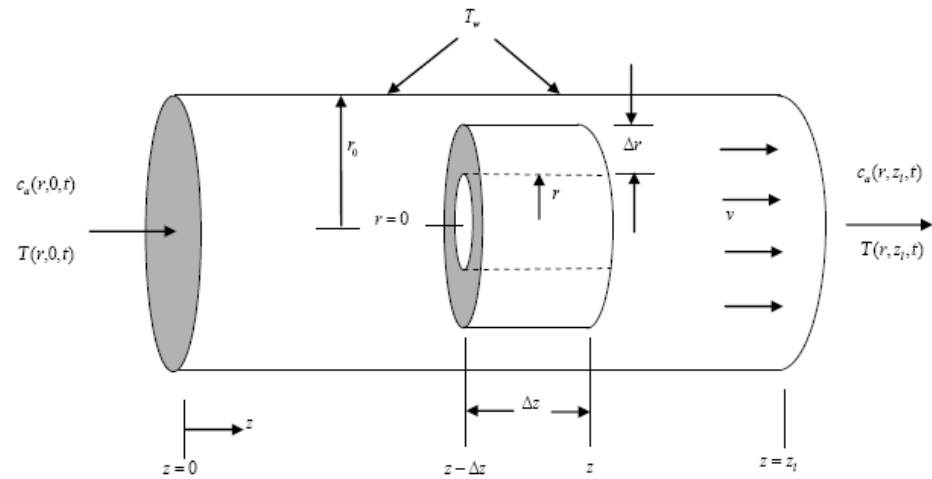
2-D pseudo homogeneous model with axial and radial dispersion

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

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

Balance element of volume





Balance equations

$$D_{ni} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + D_{ai} \frac{\partial^2 c_i}{\partial z^2} - v_z \frac{\partial c_i}{\partial z} + v_r r_r = 0$$

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

Boundary and initial conditions

$$z = 0, \quad 0 < r < r_0$$

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

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

$$r = r_0$$

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

$$r = 0$$

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

Fluidized bed catalytic reactor

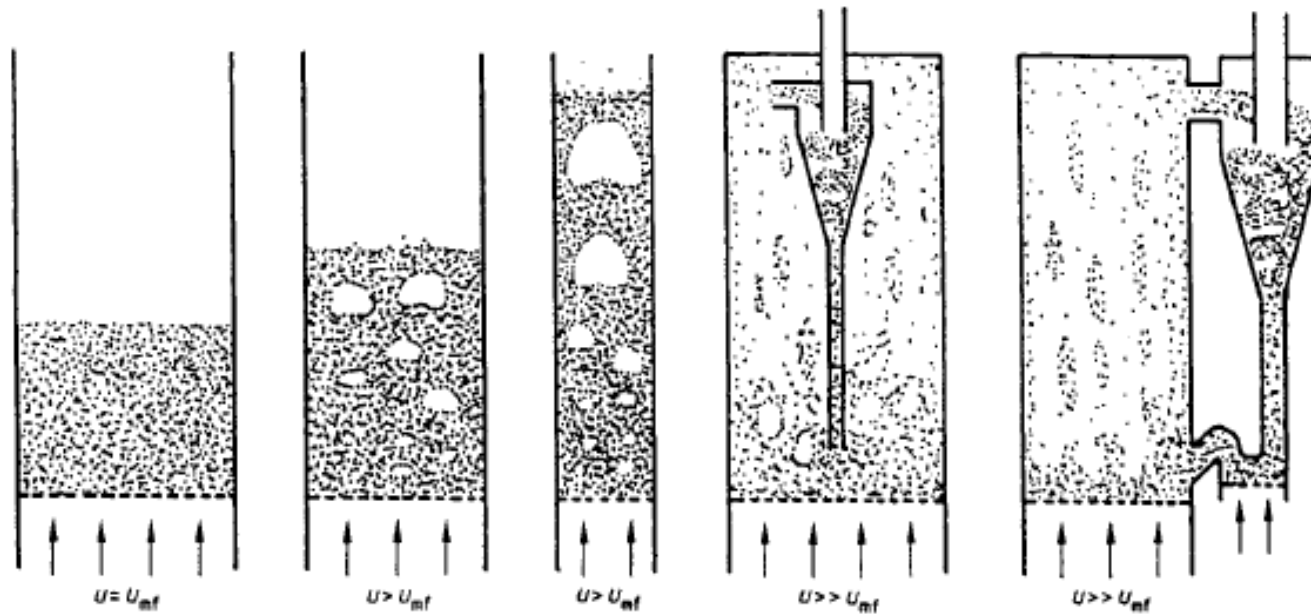


Figure 2. Forms of gas-solids fluidized beds.

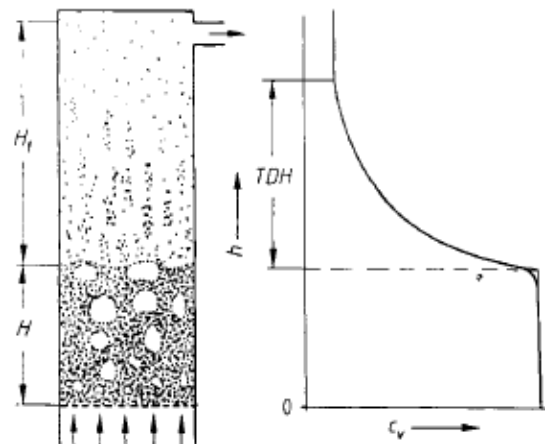


Figure 7. Schematic drawing of fluidized bed and freeboard.

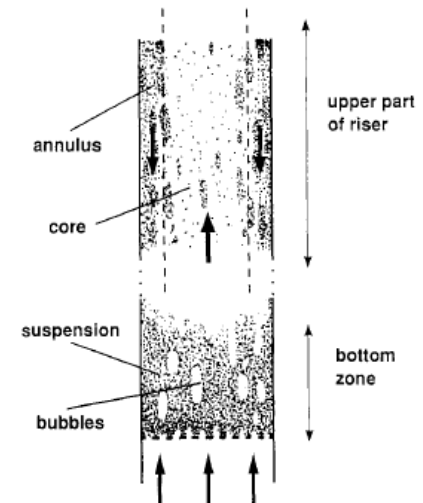


Figure 9. Schematic diagram of flow structure in a circulating fluidized bed.

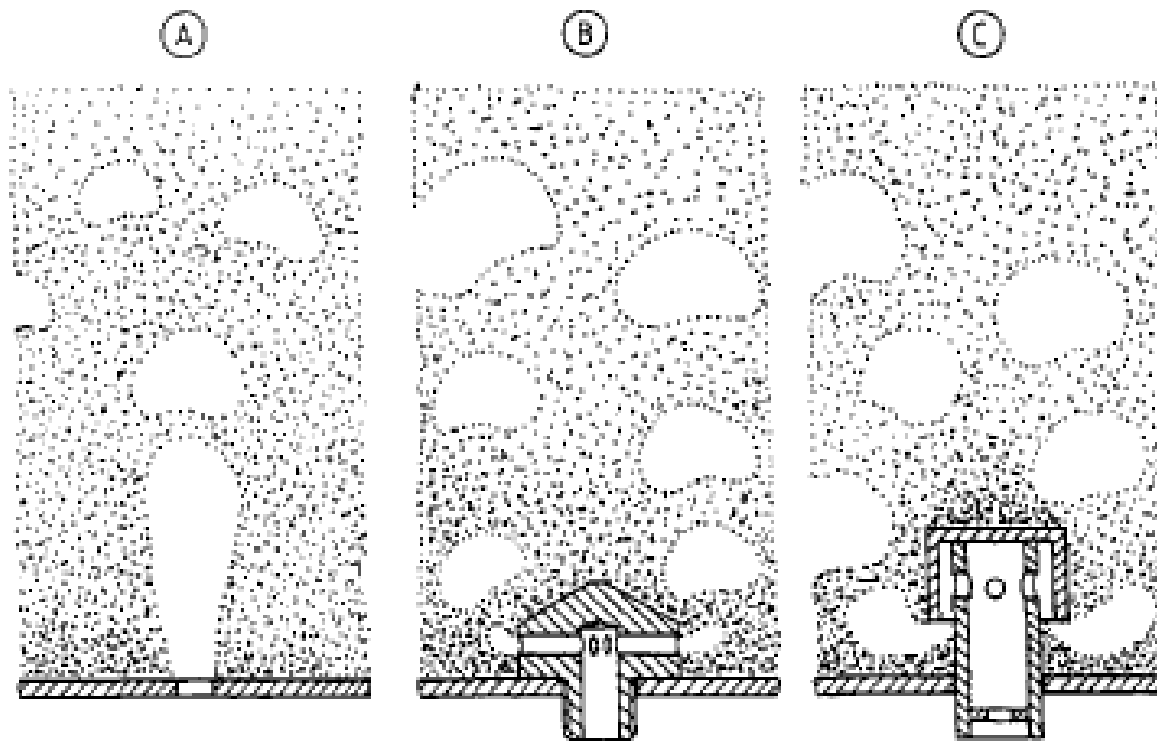


Figure 4. Industrial gas distributors: (A) perforated plate; (B) nozzle plate; (C) bubble-cap plate.

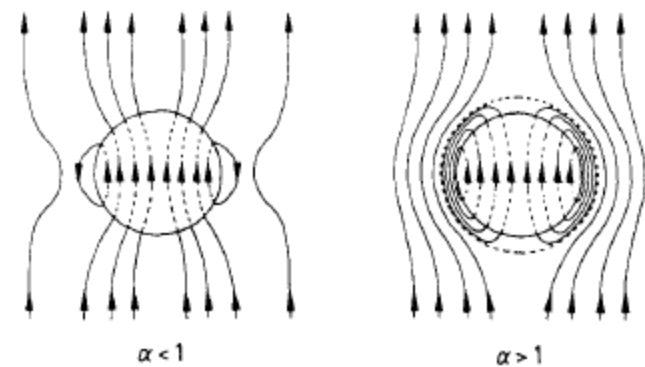


Figure 5. Gas flow for isolated rising bubbles in the Davidson model [30].

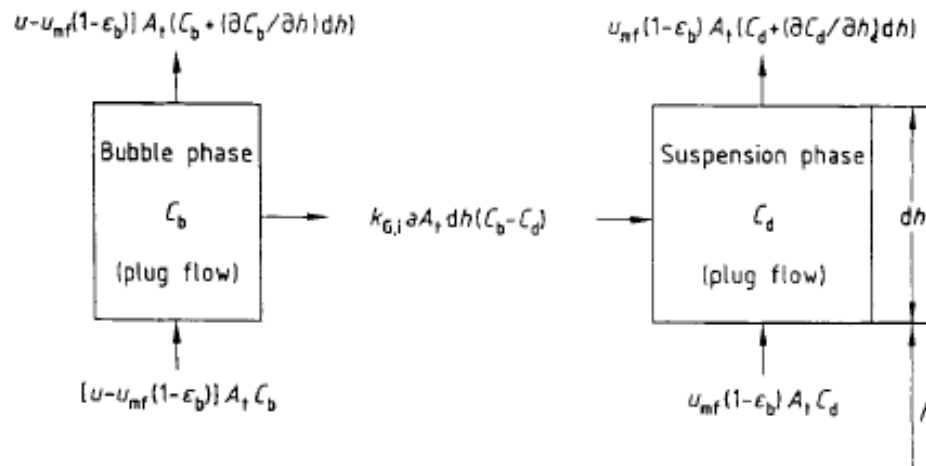


Figure 20. Two-phase model of the fluidized-bed reactor.

$$\varepsilon_b \frac{\partial C_{bi}}{\partial t} = -[u - u_{mf}(1 - \varepsilon_b)] \times \frac{\partial C_{bi}}{\partial h} - k_{G,i} \times a \times (C_{bi} - C_{di}) \quad (26)$$

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

$$a = \frac{6\varepsilon_b}{d_v} \quad (28)$$

Experimental determination of kinetics of heterogeneous catalytic reactions



OVERVIEW

1. Steady state techniques

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1.2 Transport Disguises at Particle Scale

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2.1 Dynamical Changes in catalysts: Reaction Sites, Structure and Morphology, Surface Composition

2.2 Modes of Operation: Steps and Pulses, Cycled Feed, Self-sustained Oscillations, TAP, SSITKA

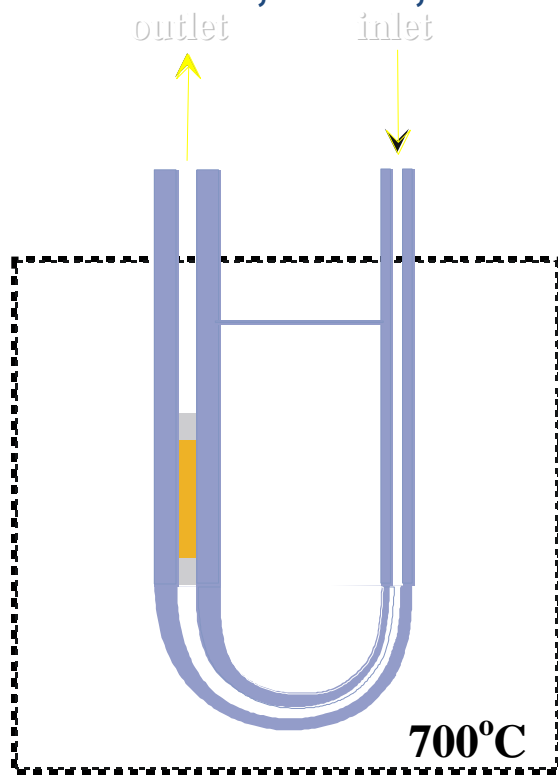
2.3 Modelling and estimation: CO chemisorption on Pt, NO reduction by H_2 , Electrocatalytic Ethylene Epoxidation, CO methanation

1. Steady state techniques

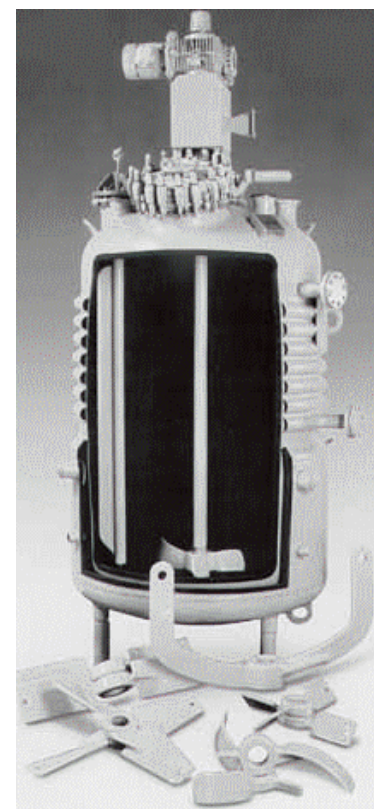
1.1 Reactors: Batch, CSTR, PFR

Screening of catalysts – high throughput methods - most promising formulation investigated in more detail – scale up of the catalytic reaction towards the industrial application starts from the knowledge of detailed reaction kinetics \Rightarrow rate equation(s)

Batch reactor, CSTR, PFR



- reactor
- catalyst
- silica wadding
- furnace



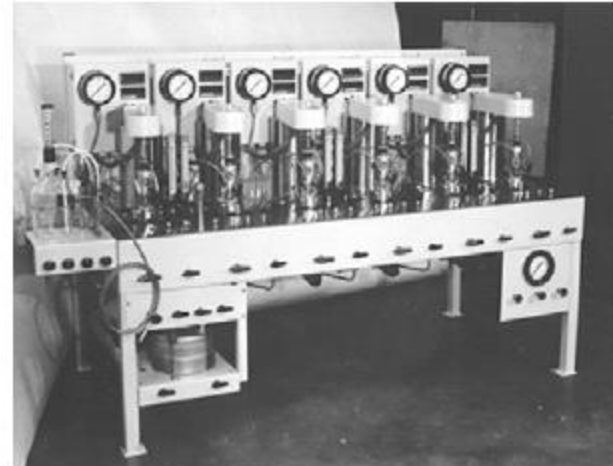


Figure 1.17. Batch reactors : a) glass, b) high pressure, c) in parallel mode.

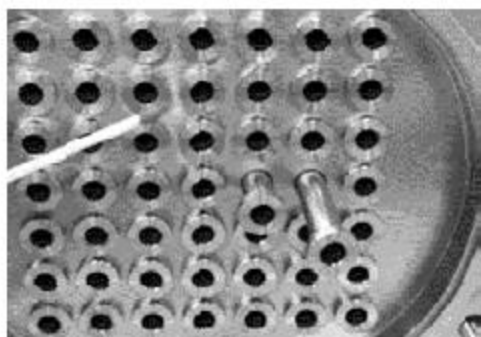


Figure 1.21. Multitubular reactor.

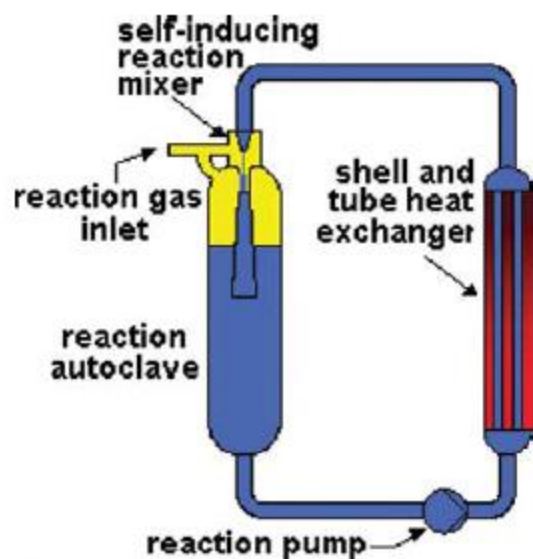


Figure 1.26. The Buss loop reactor

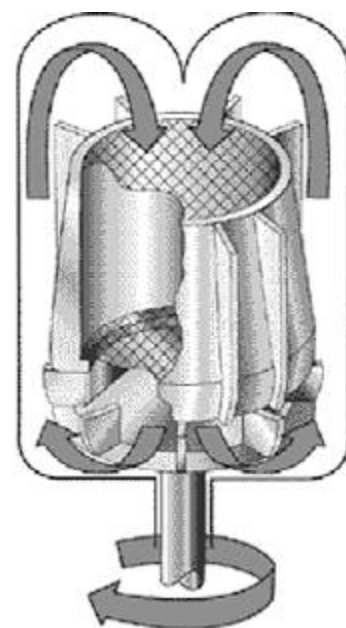


Figure 1.27. Berty gradientless reactors

Calculation of reaction rate r [mol/kg/s]

CSTR

+ direct evaluation of r.r.

-outlet condition's control

-real hydrodynamics
differentiation

PFR

+simple setup

+variation of m/F

-temperature and conc.gradients -

-isothermicity

-differentiation in r.r. calculation

BATCH

+simple setup

-isothermicity

$$r_M = \frac{F_A^o X_A}{|v_A| m}$$

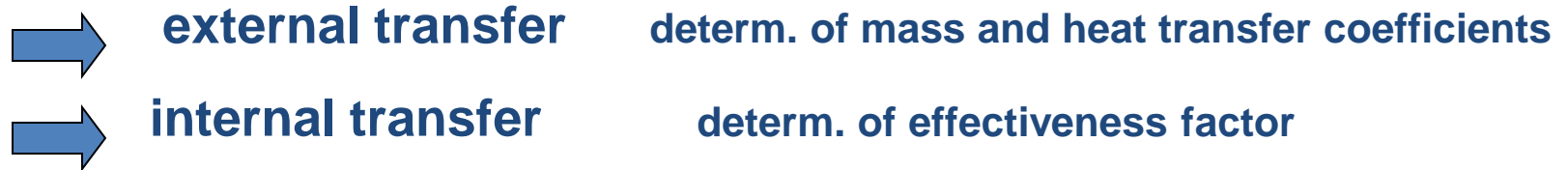
$$r_M = \frac{1}{|v_A|} \frac{dX_A}{d(m / F_A^o)}$$

$$r_M = \frac{1}{|v_A|} \frac{n_A^o}{m} \frac{dX_A}{dt}$$

$$X_A = \frac{F_A^o - F_A}{F_A^o}$$

1.2 Transport Disguises at Particle Scale

Ideality at reactor scale (plug flow or ideal mixing), it is not sufficient to obtain accurate kinetic data



$$Sh_i = \frac{k_i^o L}{D_{mi}} \quad \text{external transfer}$$

Deska

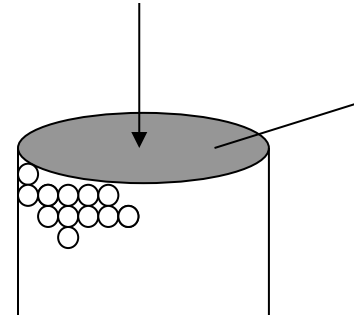
$$\text{Re}_L < 10^5 \quad Sh_i = 0,66 \text{Re}_L^{1/2} Sc_i^{1/3} \quad \text{Re}_L = \frac{uL}{\nu} \quad Sc_i = \frac{D_{mi}}{\nu}$$

$$\text{Re}_L > 10^5 \quad Sh_i = 0,036 \text{Re}_L^{0,8} Sc_i^{1/3}$$

Koule

$$Sh_i = 2,0 + 0,4(\text{Re}_L^{1/2} + 0,06 \text{Re}_L^{2/3}) Sc_i^{0,4}$$

Packed bed



$$j_D = \frac{k_{ci}^o \bar{M}}{G} Sc_i^{2/3}$$

$$Sc_i = \frac{\mu}{\rho D_{im}} \quad G = \frac{\dot{m}}{S_o} \quad Re = \frac{d_p G}{\mu}$$

$$j_D = f(Re) = C \cdot Re^n$$

$$j_H = \frac{h}{\bar{C}_p G} Pr^{2/3}$$

$$Pr = \frac{\bar{C}_{pm} \mu_m}{\lambda_m}$$

$$j_H = f(Re) = C' Re^{n'}$$

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

$$\frac{T_s}{T_o} - 1 = (-\Delta H_r) \frac{k_{xA} x_A^o}{h T_o} \left(1 - \frac{x_A^s}{x_A^o}\right)$$

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

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

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

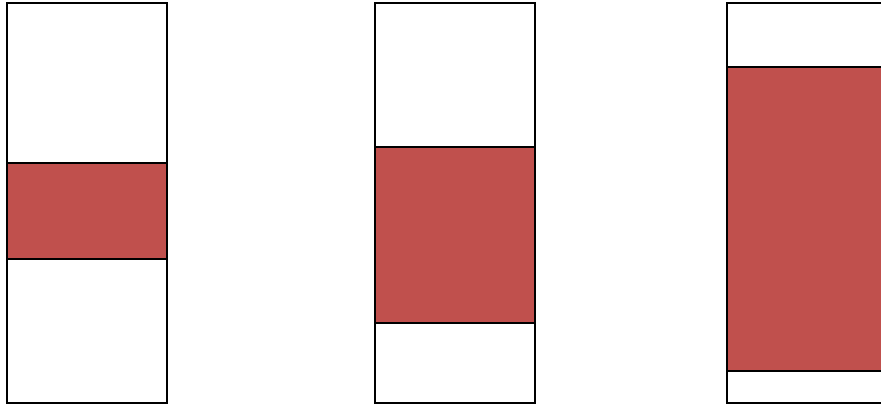
$$\frac{T_s}{T_o} - 1 = (-\Delta H_r) \frac{k_{xA} x_A^o}{h T_o} \left(1 - \frac{x_A^s}{x_A^o}\right)$$

Criteria for the absence of transport limitations (packed bed)

$$\frac{|c_A^s - c_A^o|}{c_A^o} \geq 0,95$$

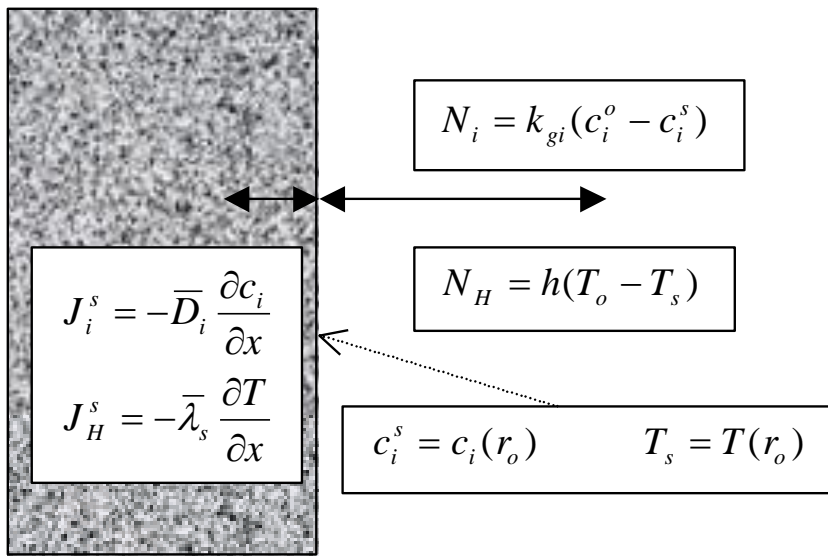
$$\frac{T_s - T_o}{T_o} \leq 0,02$$

Experimental tests



$$m / F_A^o = konst$$



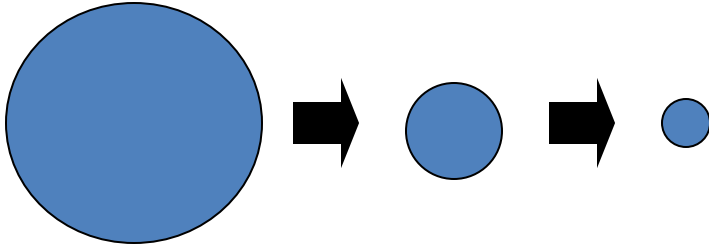


$$\frac{\Delta T}{T(r_o)} = \frac{(-\Delta H_r) \bar{D}_i c_i(r_o)}{|v_i| \bar{\lambda}_s T(r_o)} \frac{\Delta c_i}{c_i(r_o)} = \beta_i \frac{\Delta c_i}{c_i(r_o)}$$

β_i – Prater number

$\bar{D}_i \left(\frac{d^2 c_i}{dx^2} + \frac{a}{x} \frac{dc_i}{dx} \right) = -v_i r_V(T, c_k)$		
$\bar{\lambda}_s \left(\frac{d^2 T}{dx^2} + \frac{a}{x} \frac{dT}{dx} \right) = (-\Delta H_r) r_V(T, c_k)$		
$a = \begin{matrix} 0 & \text{plate} \\ 1 & \text{cylinder} \\ 2 & \text{sphere} \end{matrix}$		
$x = 0 \qquad \qquad \qquad x = r_o$		
$\frac{dc_i}{dx} = 0 \qquad \frac{dT}{dx} = 0 \qquad -\bar{D}_i \frac{dc_i}{dx} = k_{gi}(c_i^o - c_i^s)$		
$\qquad \qquad \qquad -\bar{\lambda}_s \frac{dT}{dx} = h(T_o - T_s)$		

Experimental tests (supposing that external gradients are negligible)

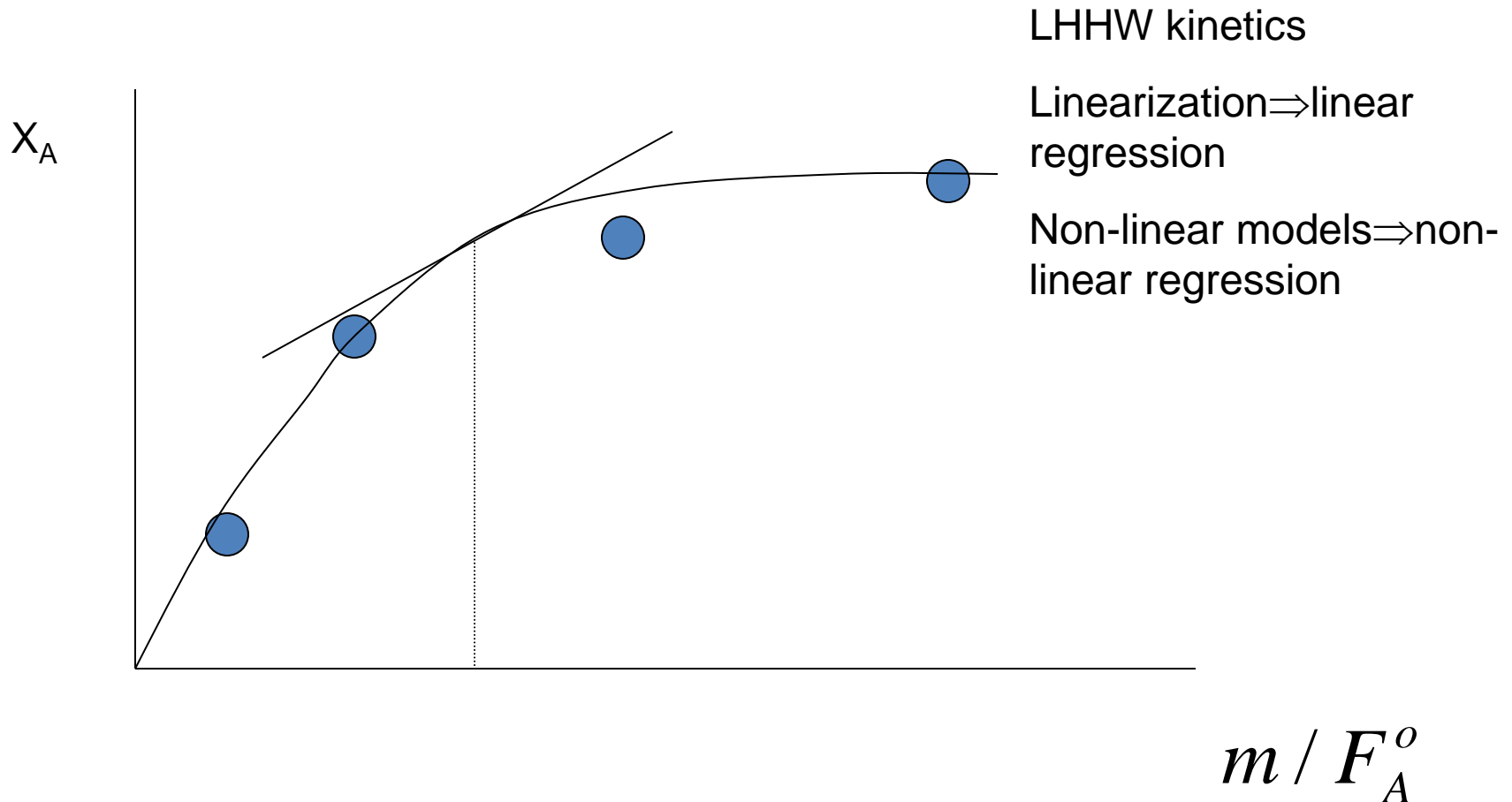


$$m / F_A^o = konst$$



1.3 Kinetic Analysis : Single Reaction, Complex Reactions, Estimation Methods

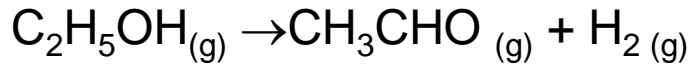
The differential or integral method of kinetic analysis



Example

Ethanol dehydrogenation (Franckaerts, Froment, 1964)

$A \rightarrow R + S$



r.d.s.

Adsorption of A

$$r_M = \frac{k_A(P_A - P_R P_S / K)}{1 + \frac{K_A}{K} P_R P_S + K_R P_R + K_S P_S + K_w P_w}$$

Surface reaction

$$r_M = \frac{k K_A (P_A - P_R P_S / K)}{(1 + K_A P_A + K_R P_R + K_S P_S + K_w P_w)^2}$$

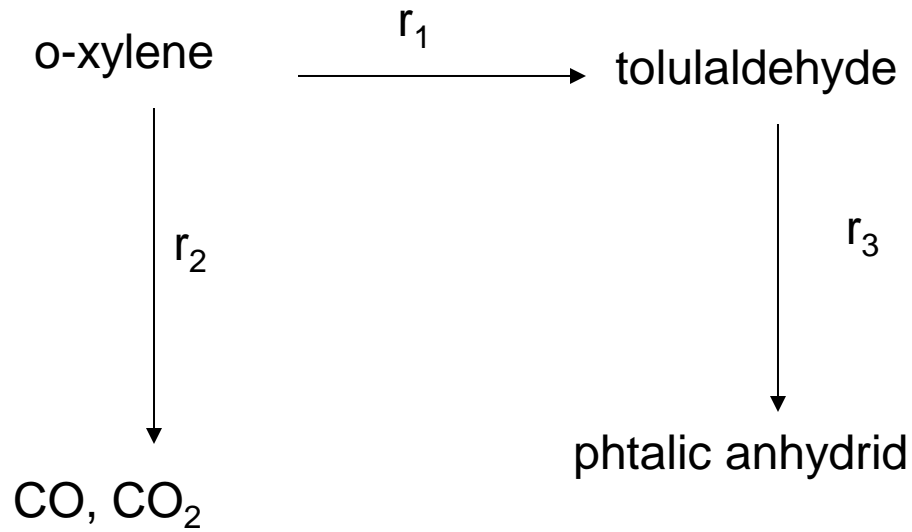
Desorption of R

$$r_M = \frac{k_R K K_R (P_A / P_S - P_R / K)}{1 + K_A P_A + K K_R P_A / P_S + K_S P_S + K_w P_w}$$

$$\Phi(\vec{\beta}) = \sum_{i=1}^M [X_i - f_i(\vec{\beta})]^2$$

Example

Air oxidation of o-xylene on V_2O_5 (Vanhove, Froment 1975)



Estimation methods

$$\mathbf{y} = \mathbf{f}(\mathbf{x}, \boldsymbol{\beta})$$

$$\mathbf{e}_j(\boldsymbol{\beta}) = \mathbf{y}_j - \mathbf{f}(\mathbf{x}_j, \boldsymbol{\beta}) \quad j = 1, NEXP$$

Moment matrix of residuals

$$\mathbf{M}(\boldsymbol{\beta}) = \sum_{j=1}^{NEXP} \mathbf{e}_j(\boldsymbol{\beta}) \mathbf{e}_j(\boldsymbol{\beta})^T$$

Gradient, Gauss-Newton

Objective functions

$$\Phi(\boldsymbol{\beta}) = \text{Trace}[\mathbf{Q}\mathbf{M}(\boldsymbol{\beta})]$$

Marquardt-Levenberg

$$\Phi(\boldsymbol{\beta}) = \text{Trace}[\mathbf{V}^{-1}\mathbf{M}(\boldsymbol{\beta})]$$

Quadratic expansion

$$\Phi(\boldsymbol{\beta}) = \det[\mathbf{M}(\boldsymbol{\beta})]$$

2. Transient methods

Reaction sites - single crystal surfaces, ultra high vacuum
⇒ structure sensitive reaction rate (Dahl et al. 1999: rate of dissociative adsorption of nitrogen on Ru (0001) surface was reduced by more than nine orders.

Structure and Morphology – CO oxidation on the Pt(110) surface. Ertl (1994) has shown by photo-emission electron microscopy that surface concentrations of reacting species vary with time and 2D-space.

Grunwaldt (2000) found that structure of Cu particles depend on the reduction potential of gas mixture CO+H₂.

Surface composition – surface composition of catalyst may change with gas composition – redox systems (Mars, Krevelen, 1953)