Heterogeneous non catalytic reactions

- 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

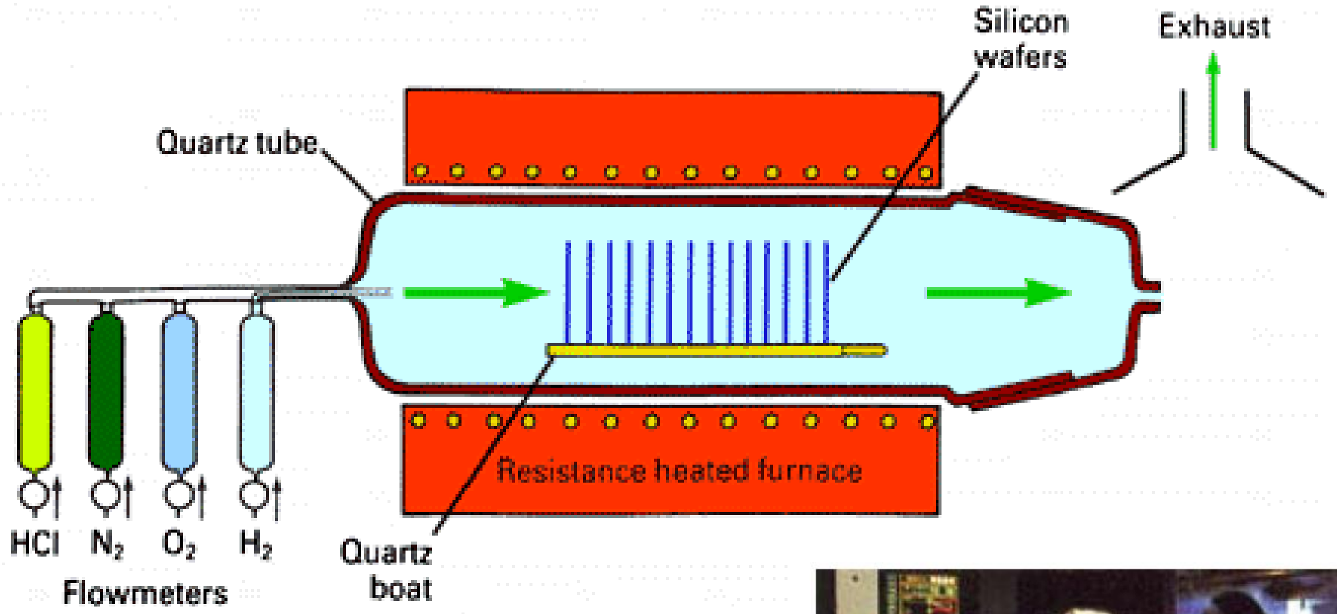
➢ $CoO_{(s)} + Al_2O_{3(s)} \rightarrow CoAl_2O_{4(s)}$

Heat and mass transfer phenomena affect global reaction rate.

Heterogeneous gas-solid reactions

$$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$$

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

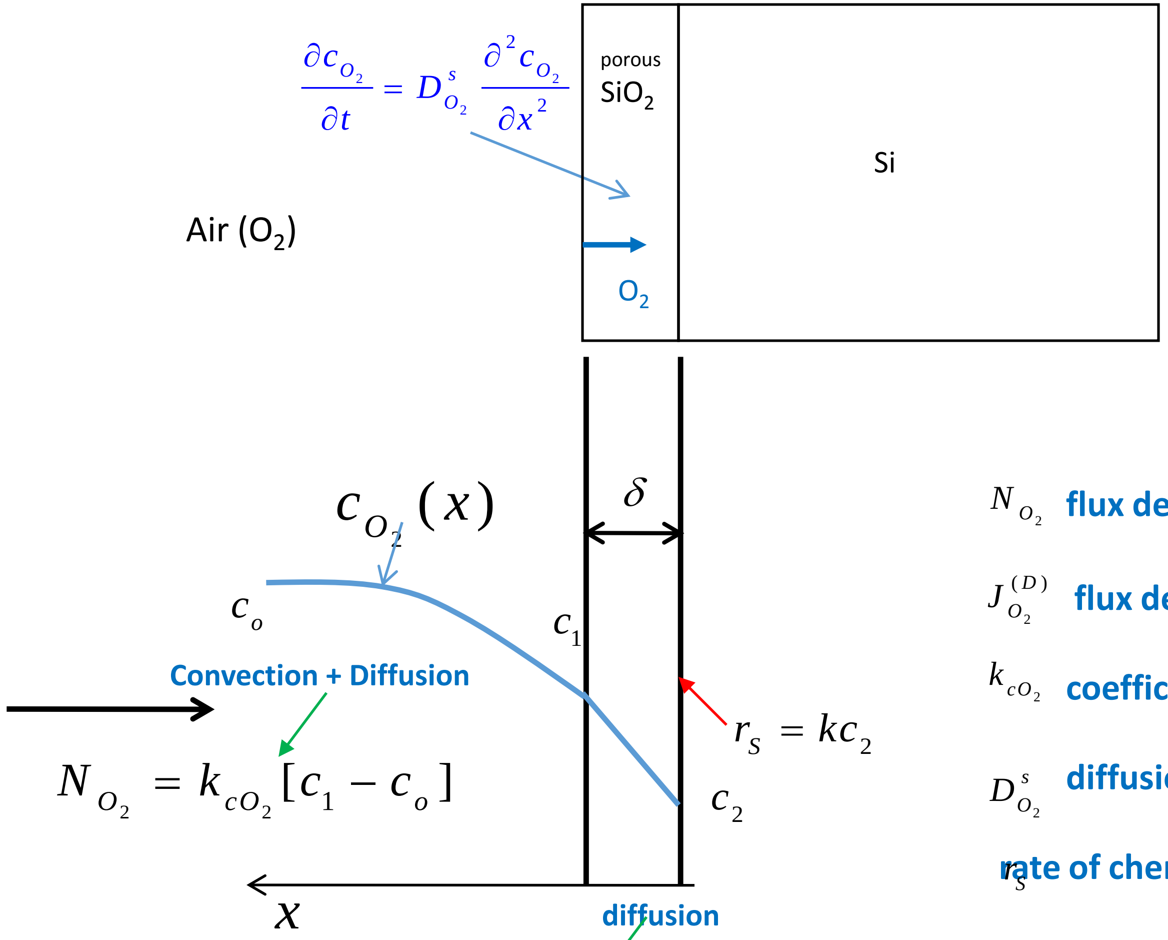


Oxidation Furnace
(Silicon Valley Group - Thermco Systems)

Kinetics of gas-solid heterogeneous reaction

$$Si_{(s)} + O_{2(g)} \rightarrow SiO_{2(s)}$$

$$\frac{\partial c_{O_2}}{\partial t} = D^s_{O_2} \frac{\partial^2 c_{O_2}}{\partial x^2}$$



$$N_{O_2} = k_{cO_2}[c_1 - c_o]$$

$$J^{(D)}_{O_2} = -D^s_{O_2}\frac{dc_{O_2}}{dx} \cong D^s_{O_2}\frac{[c_2 - c_1]}{\delta}$$

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

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

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

$D^s_{O_2}$ diffusion coefficient of O_2 in SiO_2 (m^2.s^{-1})

r_S rate of chemical reaction (mol. m^{-2}.s^{-1})

Steady state

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

$$k_{cO_2}[c_1 - c_o] = D_{O_2}^s \frac{[c_2 - c_1]}{\delta} = -kc_2$$

c_1 a c_2 calculation :

$$\left(k_{cO_2} + \frac{D_{O_2}^s}{\delta}\right)c_1 - \frac{D_{O_2}^s}{\delta}c_2 = k_{cO_2}c_o$$

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

$$\Longrightarrow$$

$$c_1 = \frac{k_{cO_2}\left(k + \frac{D_{O_2}^s}{\delta}\right)}{k.k_{cO_2} + \frac{D_{O_2}^s}{\delta}(k_{cO_2} + k)}c_o$$

$$c_2 = \frac{k_{cO_2}\frac{D_{O_2}^s}{\delta}}{k.k_{cO_2} + \frac{D_{O_2}^s}{\delta}(k_{cO_2} + k)}c_o$$

reaction rate

$$r_s = \frac{c_o}{\frac{1}{k_{cO_2}} + \frac{\delta(t)}{D_{O_2}^s} + \frac{1}{k}}$$

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

SiO_2 layer thickness and Si conversion :

$$\left[\frac{1}{k_{cO_2}} + \frac{1}{k}\right]\delta + \frac{1}{2}\frac{\delta^2}{D_{O_2}^s} = c_o \frac{M_{SiO_2}}{\rho_{SiO_2}}t$$

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

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

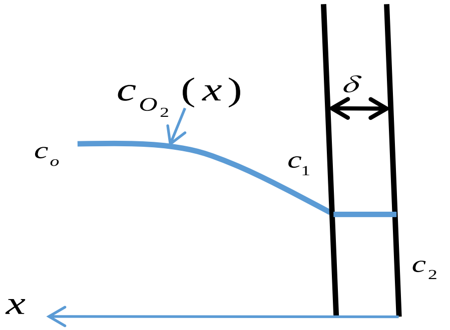
$M_{SiO_2}, M_{Si}, \rho_{SiO_2}, \rho_{Si}$ **Molar weights and densities of SiO_2 a Si**

δ_o **Initial thickness of Si slab**

3 limiting cases

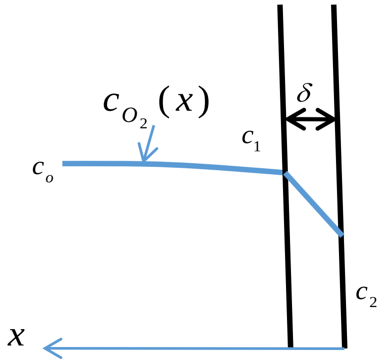
1. Rate determining step is the external mass transfer of oxygen towards interface (gas - SiO_2)

$$\frac{1}{k_{cO_2}} >> \frac{\delta}{D^s_{O_2}}, \frac{1}{k_{cO_2}} >> \frac{1}{k} \Rightarrow r_s = k_{cO_2} c_o, \qquad \delta = k_{cO_2} c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$



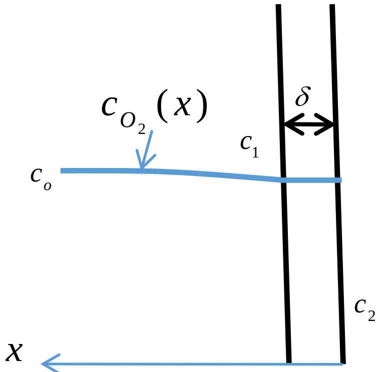
2. Rate determining step is the internal mass transfer of oxygen in porous SiO_2 layer

$$\frac{\delta}{D^s_{O_2}} >> \frac{1}{k_{cO_2}}, \frac{\delta}{D^s_{O_2}} >> \frac{1}{k} \Rightarrow r_s = \frac{D^s_{O_2}}{\delta} c_o, \qquad \delta = \sqrt{2 D^s_{O_2} c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t}$$



3. Rate determining step is chemical reaction taking place on the interface (SiO_2 - Si)

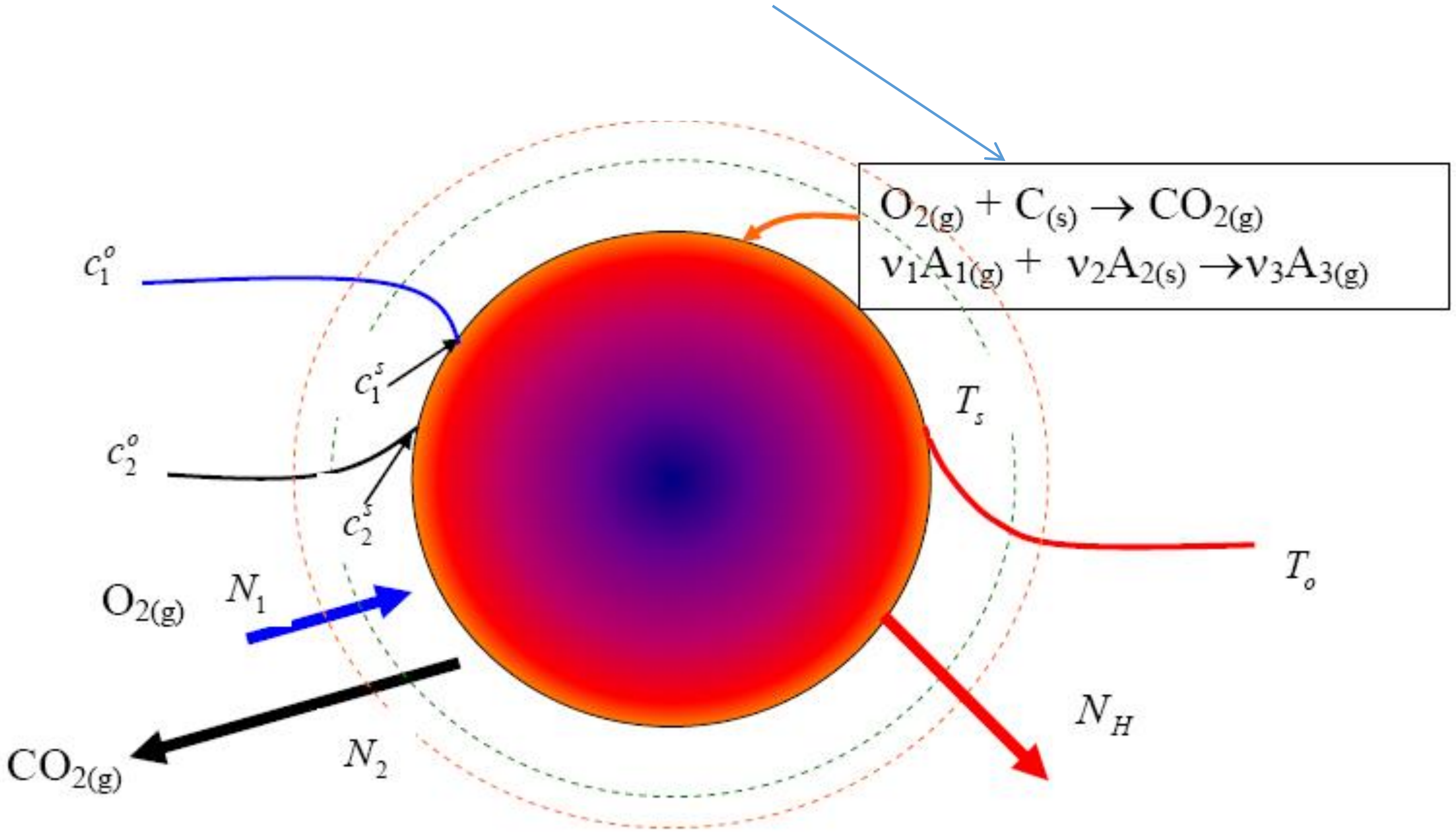
$$\frac{1}{k} >> \frac{\delta}{D^s_{O_2}}, \frac{1}{k} >> \frac{1}{k_{cO_2}} \Rightarrow r_s = k c_o, \qquad \delta = k c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t$$



Discussion: r_S = f(composition), r_S = f(temperature)

External heat and mass transfer

Combustion of the spherical carbon particle



Conditions in the immediate region of an interface between phases are hard to explore experimentally. In such situations it is helpful to develop a mathematical model of the process starting with the known basic facts. The result of the analysis is then compared with those experimental measurements which it is possible to make. Good agreement suggests that the model may have been realistic.
—T. K. Sherwood, R. L. Pigford, and C. R. Wilke (1975)

Oxygen molar flux at steady state

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

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

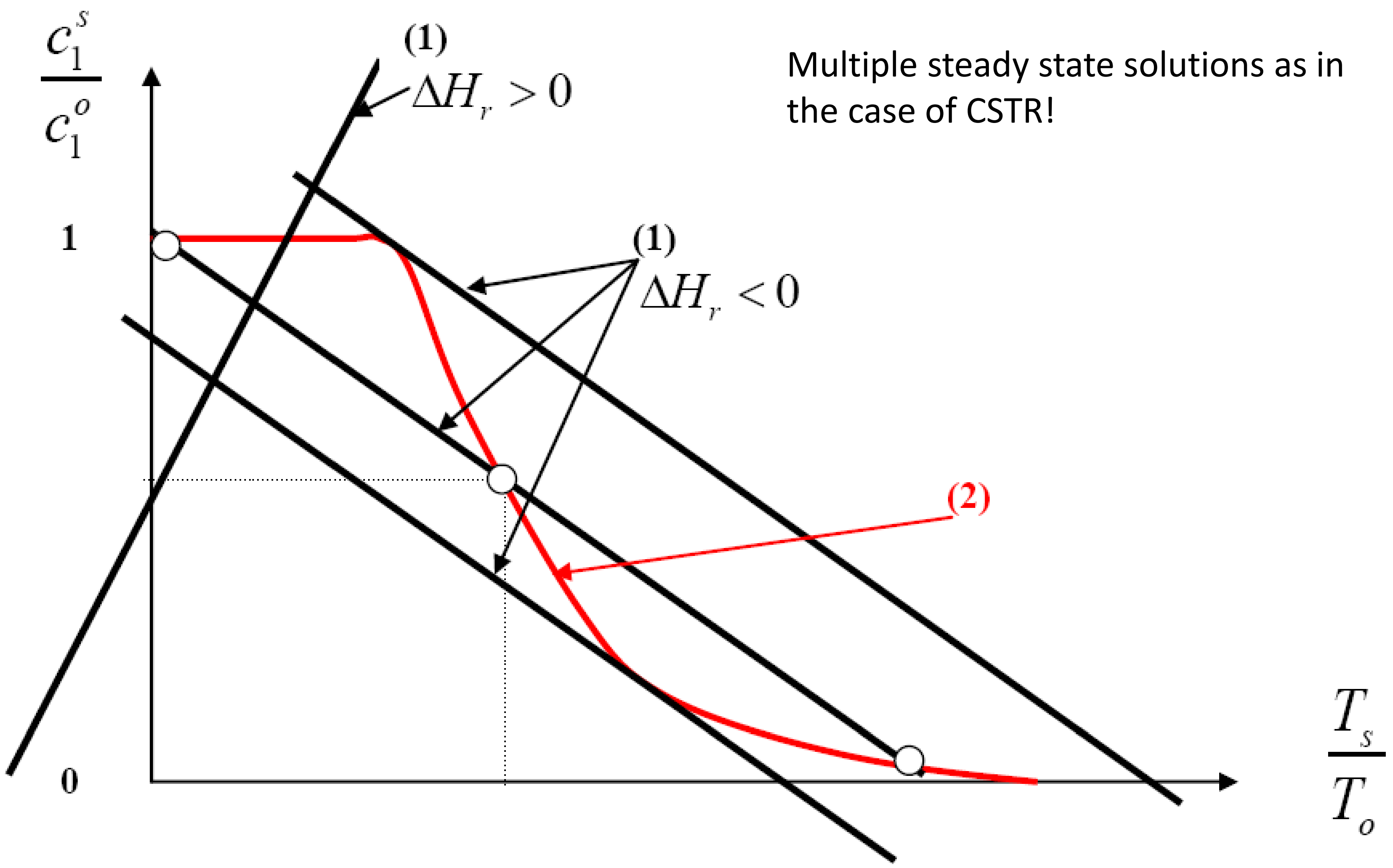
$$ha(T_s - T_o) = (-\Delta H_r) r_V = (-\Delta H_r) k_{c1} a (c_1^o - c_1^s)$$

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

$$k_{c1} a (c_1^o - c_1^s) = k(T_s) \left(c_1^s\right)^n$$

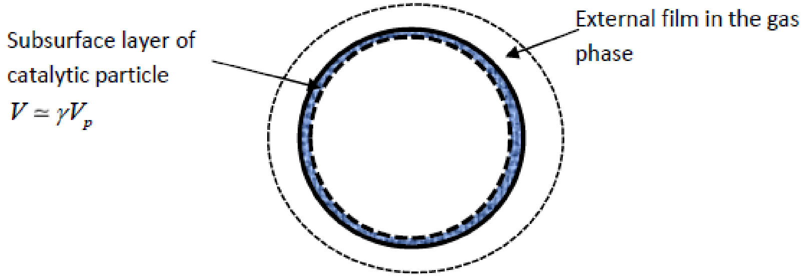
$$n = 1$$

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



Multiple steady state solutions as in the case of CSTR!

Example



Molar material balances

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

Enthalpy balance

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

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

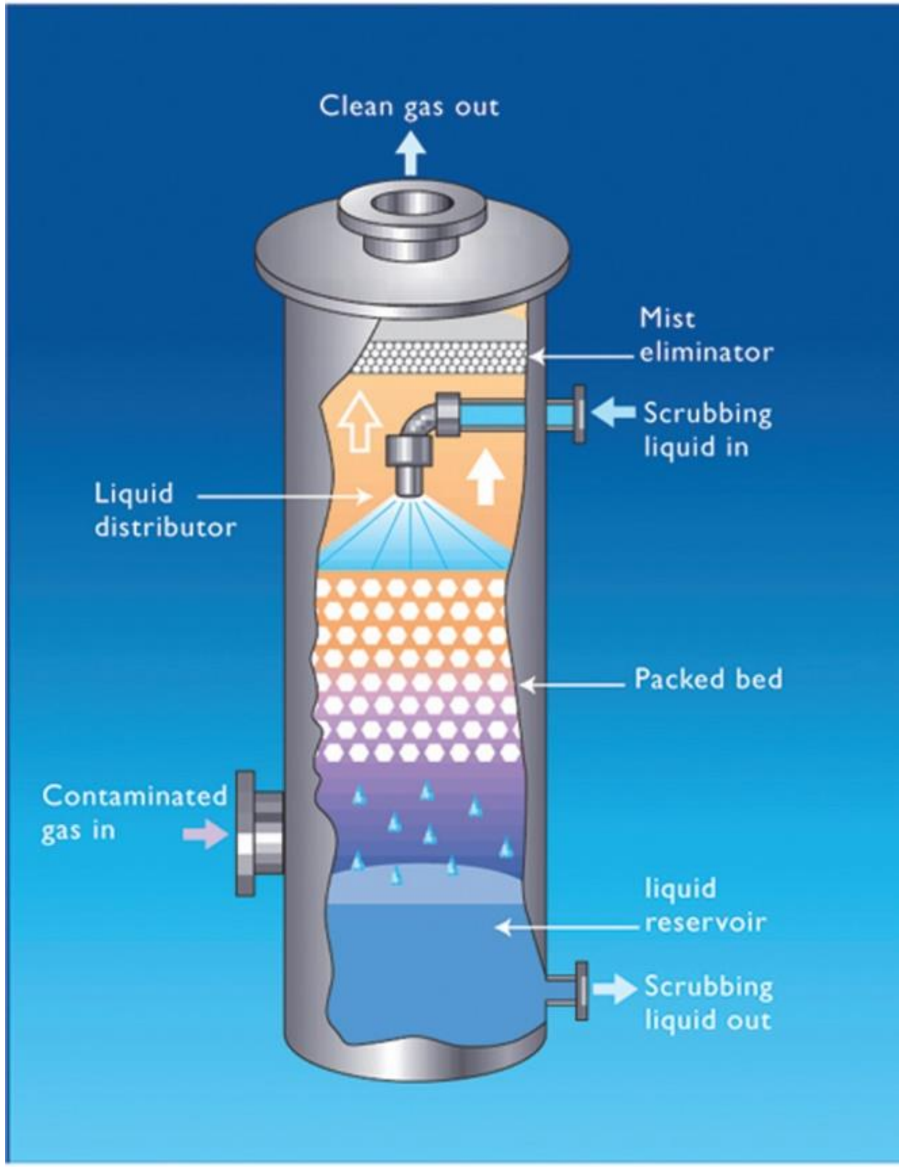
$NH_3 + 1.25O_2 \rightarrow NO + 1.5H_2O$ $\quad \Delta_r H_1 = -226.66$ kJ.mol^{-1} (1)

$NH_3 + 0.75O_2 \rightarrow 0.5\,N_2 + 1.5H_2O$ $\quad \Delta_r H_2 = -275.22$ kJ.mol^{-1} (2)

$NH_3 + O_2 \rightarrow 0.5N_2O + 1.5H_2O$ $\quad \Delta_r H_3 = -317.10$ kJ.mol^{-1} (3)

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

Heterogeneous gas-liquid reactions



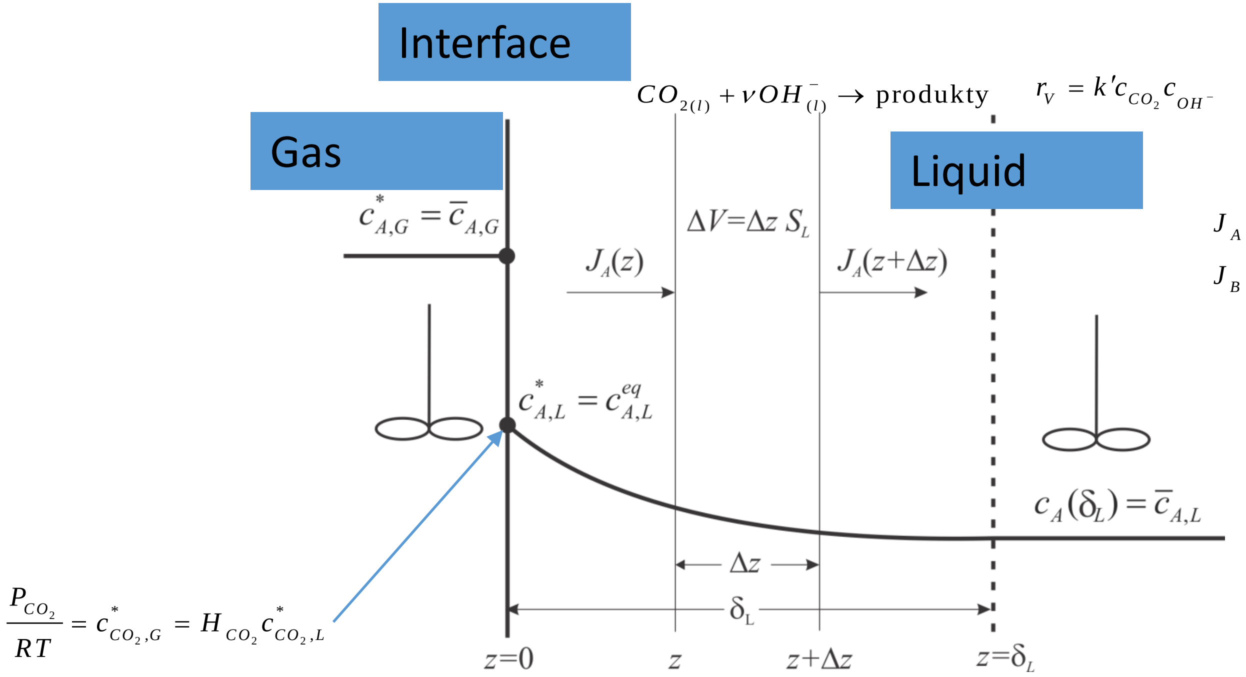
Kinetics of gas-liquid reactions

$$CO_{2(g)} \rightleftarrows CO_{2(l)} \left(CO_{2(l)} = A \right)$$

$$CO_{2(l)} + OH^-_{(l)} \rightleftarrows HCO^-_{3(l)} \left(OH^-_{(l)} = B \right)$$

$$HCO^-_{3(l)} + OH^-_{(l)} \rightleftarrows CO^{2-}_{3(l)} + H_2O_{(l)}$$

$$CO_{2(l)} + \nu OH^-_{(l)} \rightarrow \text{produkty} \qquad r_V = k' c_{CO_2} c_{OH^-} \qquad \left(\text{mol.m}^{-3}.\text{s}^{-1}\right)$$



$$J_A(z+\Delta z)S_L = J_A(z)S_L - r_V \Delta z S_L$$

$$J_B(z+\Delta z)S_L = J_B(z)S_L - |\nu| r_V \Delta z S_L$$

$$J_A = -D_A \frac{dc_A}{dz}$$

$$J_B = -D_B \frac{dc_B}{dz}$$

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

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

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

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

Boundary conditions

$$z = 0 : c_A = c_{A,L}^{eq}, \frac{dc_B}{dz} = 0$$

or

$$z = 0; -D_A \frac{dc_A}{dz} = k_{cA,G}\left(\bar{c}_{A,G} - c_{A,G}^{*}\right) = k_{cA,G}\left(\bar{c}_{A,G} - H_A c_A (z = 0)\right), \frac{dc_B}{dz} = 0$$

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

Dimensionless form

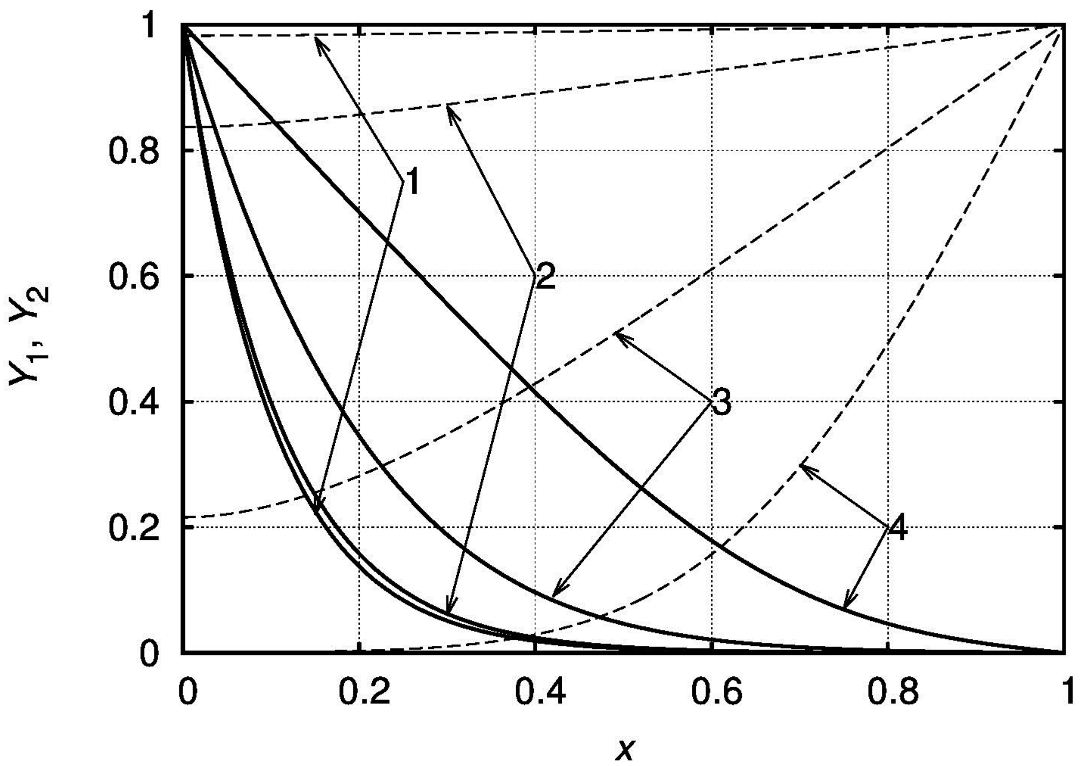
$$x = \frac{z}{\delta_L}, Y_1 = \frac{c_{CO_2}}{c_{CO_2,L}^{eq}} = \frac{c_A}{c_{A,L}^{eq}}, Y_2 = \frac{c_{OH^-}}{\bar{c}_{OH^-,L}} = \frac{c_B}{\bar{c}_{B,L}}$$

$$\frac{d^2 Y_1}{dx^2} - \mathrm{Ha}^2 Y_1 Y_2 = 0 \qquad \frac{d^2 Y_2}{dx^2} - \chi\, \mathrm{Ha}^2 Y_1 Y_2 = 0$$

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

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

Numerical solution gives to us concentration profiles

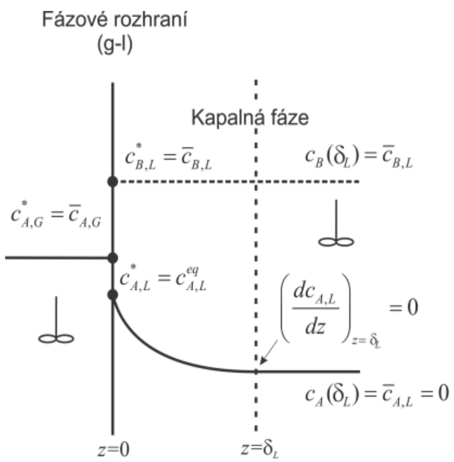


We get the overall rate of CO2 absorption by integration of local rate

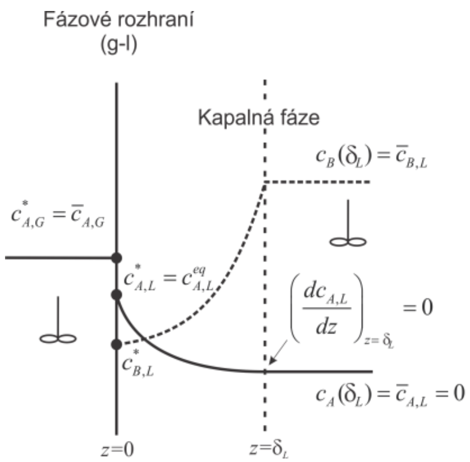
$$R_A = -\frac{1}{V_L}\int_0^{V_L} r_V \, dV \qquad -\left[-S_L D_A \left(\frac{dc_A}{dz}\right)_{z=0}\right] = V_L R_A \qquad \frac{S_L D_A c_{A,L}^{eq}}{V_L \delta_L}\left(\frac{dY_1}{dx}\right)_{x=0} = R_A$$

Limiting situations

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



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



$$Ha > 3$$