**EXAMPLE 3.2-3 Heterogeneous Reaction in a Binary Gas** This example illustrates the use of Fick's law for a binary gas and also shows how the reaction kinetics can influence the boundary condition at a catalytic surface. The system to be considered is shown in Fig. 3-5. A stagnant gas film of thickness $L$ is in contact with a surface that catalyzes the irreversible reaction $A \to mB$. The catalyst is impermeable to $A$ and $B$. The reaction rate at the solid surface ($y = L$) is assumed to follow $n$th-order kinetics,

Reaction rate:

$$-N_A\Big|_{y=L} = R_{SA} = -k_{sn}[C_A(L)]^n \quad ; \quad k_{sn} \text{ mass transfer coeff} \tag{3.2-29}$$

where $n > 0$ and $k_{sn}$ is a constant. It is assumed that $C_A$ depends on $y$ only and that its value at $y = 0$ is $C_0$. It is assumed also that the gas is isothermal and isobaric, so that the total molar concentration ($C$) is constant. Unless the molecular weights of $A$ and $B$ are identical (i.e., unless $m = 1$), the total mass density ($\rho$) will not be constant. It is desired to determine the reaction rate.

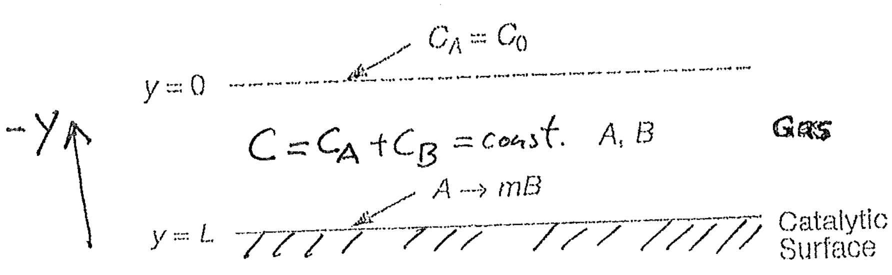



Figure 3-5. Steady diffusion in a binary gas film with an irreversible heterogeneous reaction.

Note! As the mass density $\rho$ cannot be assumed to be constant, we have to consider:

the general form of the continuity eq. $\dfrac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$

$\xrightarrow[\text{Table 2-2}]{\text{1D, s.s.}}$ $\boxed{\dfrac{d}{dy}(\rho v_y) = 0} \Rightarrow \rho v_y \neq f(y)$

as $v_y\Big|_{y=L} = 0$ (impermeability) $\Rightarrow v_y = 0$ throughout gas film

$\Rightarrow \underline{N_{iy} = J_{iy}}$ (no bulk flux)

Pseudobinary conservation eq requires $\rho$ to be constant. Thus, we cannot use it, but need an earlier form of the Species Conservation: (eq. 2.6-1): $\cancel{\dfrac{\partial C_i}{\partial t}}^{0}_{\text{s.s.}} = -\vec{\nabla} \cdot \vec{N}_i + \cancel{R_{V_i}}^{0}$ no volume reaction

$\Rightarrow \boxed{\dfrac{d}{dy} N_{Ay} = 0 = \dfrac{N_{By}}{dy}}$ further consideration of $N_{By}$ is unnecessary as $C_{By}$ is given by $C_{Ay}$

$\Rightarrow N_{Ay} \neq f(y)$

thus, evaluating anywhere, it determines $N_A$ for all $y$

Interfacial Species Balance for impermeable solid

Eq. 2.7-2: $J_{in}|_2 = R_i^{\leftarrow \text{surface reaction}} \Rightarrow \boxed{N_{By} = -m N_{Ay}}$

cont. Ex. 3.2-3

Next, we use an appropriate constitutive eq. The diffusive $J_{iy}$ form of Fick's Law is not a good choice, as it used for $\rho = \text{const.}$ For situations in which $C = \text{const.}$, we use the Fick's expression of the total flux of A

from the perspective of the molar average velocity $v_y^{(M)}$ the convective flux is

$$\boxed{N_{A_y} = \underbrace{x_A\left(N_{A_y} + N_{B_y}\right)}_{\substack{\text{convective flux}\\ = C_A v_y^{(M)}}} - \underbrace{C D_{AB}\frac{dx_A}{dy}}_{\text{diffusive flux}}}$$

We substitute the interfac. species balance

$$N_{B_y} = -m N_{A_y}$$ ; m Stoichiometric param.

into Fick's expression, which yields

$$N_{A_y} = \underbrace{x_A N_{A_y}(1-m)}_{C_A v_y^{(M)}} - C D_{AB}\frac{dx_A}{dy}$$

$$x_A = \frac{C_A}{C} \Rightarrow v_y^{(M)} = \frac{N_{A_y}(1-m)}{C}$$

(Note: $\underbrace{v_y^{(M)}}_{\text{molar average velocity}} \neq 0$ for $m > 1$, but $\underbrace{v_y}_{\text{mass average velocity}} = 0 \;\; \forall m$)

$$\Rightarrow \boxed{N_{A_y} = -\frac{D_{AB}}{\left[1 - \frac{C_A}{C}\right]\left[1-m\right]}\frac{dC_A}{dy}}$$ Constitutive Eq.

As $N_A\big|_{y=L} = -R_{SA} = k_{s_n}\left[C_A(L)\right]^n$ and $N_{A_y} \neq f(y)$

$$\Rightarrow \boxed{\frac{dC_A}{dy} = -\left(\frac{k_{sn}}{D_{AB}}\right)\left[C_A(L)\right]^n\left[1 - \frac{C_A}{C}(1-m)\right]}$$

BC: $C_A(0) = C_0$

cont. Ex 3.2-3

Using the dimensionless quantities:

scaled length/dist. scaled conc. unknown: scaled reactant conc. at catalytic interface

$$\eta = \frac{y}{L}, \quad \Theta = \frac{C_A}{C_0}, \quad \Phi = \frac{C_A}{C_0}\bigg|_{y=L}$$

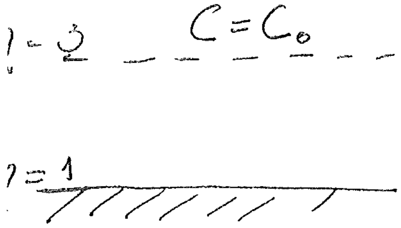
and the Damköhler number

$$Da = \frac{k_{sn} C_0^{n-1} L}{D_{AB}}$$

← reaction velocity
← diffusion velocity

Governing eq. (concentration profile)

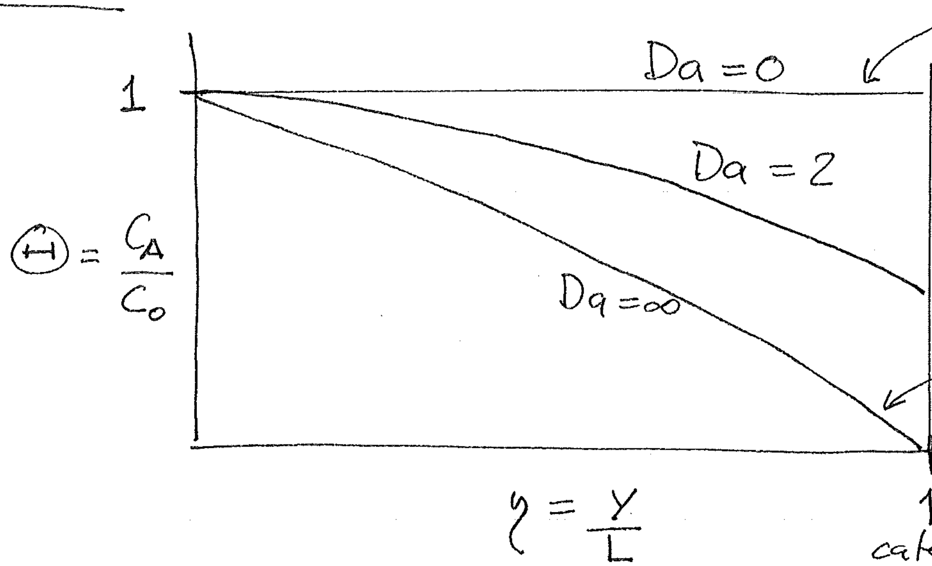
$$\Longrightarrow \quad \frac{d\Theta}{d\eta} = - Da\, \Phi^n \left[1 - x_0 (1-m)\Theta\right]$$




BC: $\Theta(0) = 1$

$x_0$ known mole fraction of A at $\eta = 0$ (stagnant film "gas interface")

Solution for $m = 1$ and $n = 1$




uniform conc. reaction is slow relative to diffusion "reaction is the controlling step"

fast reaction "the process is diffusion (mass transfer) controlled"

catalytic surface