EXAMPLE 3.2-2 Reversible Homogeneous Reaction in a Liquid This problem is similar to Example 3.2-1, except that the reaction now is reversible. Also, as shown in Fig. 3-3, the open boundary (where the concentrations are fixed at C_{A0} and C_{B0}) is now at $y = 0$ and the impermeable one is at $y = L$. The reversibility of the reaction requires that both species concentrations be considered simultaneously. Nonetheless, as will be shown, the two conservation equations can be uncoupled.

A, B in dilute stagnant liquid

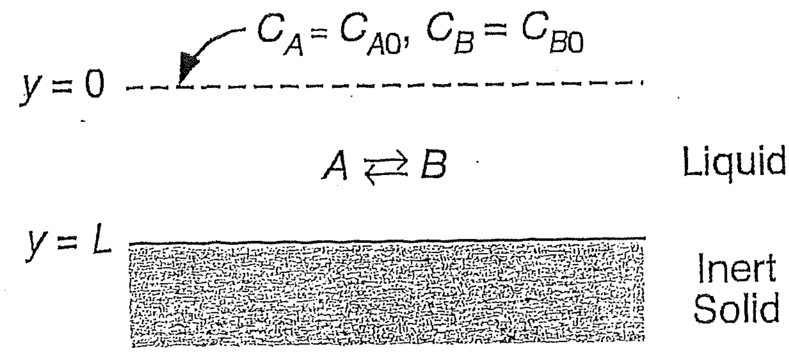

Figure 3-3. Steady diffusion in a liquid film with a reversible homogeneous reaction.

Start with same Conservation Eq. as for 3.2-1, but for both components

Coupled conserv. eq.

$$\boxed{\begin{aligned} 0 &= D_A \frac{d^2 C_A}{dy^2} + R_{VA} \\ 0 &= D_B \frac{d^2 C_B}{dy^2} + \cancel{R_{VB}}\ {-R_{VA}} \end{aligned}}$$

1st order kinetics:

$$\begin{aligned} R_{VA} &= k_{-1} C_B - k_1 C_A \\ &= k_1 (K C_B - C_A) \\ &= -R_{VB} \end{aligned}$$

equil. const: $K = \frac{+k_{-1}}{k_1}$

Boundary Conditions

BC1: $C_A(y=0) = C_{A0}$, $C_B(y=0) = C_{B0}$

BC2: $\frac{dC_A}{dy}(y=L) = 0$, $\frac{dC_B}{\partial y}(y=L) = 0$ impermeable inert solid

Sum of the two conservation eqs yields:

$$0 = D_A \frac{d^2 C_A}{dy^2} + D_B \frac{d^2 C_B}{dy^2}$$

which after integrations (twice with BCs) provides a relationship between C_A and C_B, namely:

$$\boxed{C_B(y) = \frac{D_A}{D_B}\left(C_{A0} - C_A(y)\right) + C_{B0}} \quad (*)$$

continue Ex 3.2-2

We return to our (coupled) conservation eq.

$$0 = D_A \frac{d^2 C_A(y)}{dy^2} + R_{VA} \quad ; \quad R_{VA} = k_1 \left(K\, C_B(y) - C_A \right)$$

subst (*) $\longrightarrow$

$$\Rightarrow \boxed{0 = D_A \frac{d^2 C_A}{dy^2} + k_1 \left(K \left(\frac{D_A}{D_B} \left[C_{A0} - C_A \right] + C_{B0} \right) - C_A \right)}$$

$\longrightarrow$ diff. eq. in $C_A(y)$ only

Conservation Eq.

$$0 = D_A \frac{d^2}{dy^2} C_A(y) - k_1 \left(\frac{K D_A}{D_B} + 1 \right) C_A(y) + k_1 K \left(\frac{D_A}{D_B} C_{A0} + C_{B0} \right)$$

This equation can be rewritten with the following dimensionless parameters:

Damköhler numbers for forward and backward reaction
$$= \begin{cases} \alpha \equiv \dfrac{k_1 L^2}{D_A} \\[2ex] \beta \equiv \dfrac{k_{-1} L^2}{D_B} \end{cases}$$

$$\eta = \frac{y}{L}, \quad \Theta_A = \frac{C_A}{C_{A0}}, \quad \Theta_B = \frac{K C_B}{C_{A0}}$$

Dimensionless Conservation Eq.

$$\boxed{\frac{d^2 \Theta_A}{d\eta^2} = (\alpha + \beta)\, \Theta_A - (\alpha \mu + \beta)}$$

with $\mu \equiv \dfrac{K C_{B0}}{C_{A0}}$ (determines direction of reaction) continue Ex 3.2-2

The dimensionless conservation eq. above with

$$BC(1): \quad \Theta_A(0) = 1$$

$$BC(2): \quad \frac{d\Theta_A}{d\eta}(1) = 0 \qquad \text{(impermeable solid)}$$

yields the following solutions

$$\Theta_A(\eta) = \left[\frac{\alpha\mu+\beta}{\alpha+\beta}\right] + \left[\frac{\alpha(1-\mu)}{\alpha+\beta}\right] \times$$

$$\times \left[\cosh\left(\eta\sqrt{\alpha+\beta}\right) - \tanh\left(\sqrt{\alpha+\beta}\right)\sinh\left(\eta\sqrt{\alpha+\beta}\right)\right]$$

and analoguous for $\Theta_B(\eta)$ (see text eq. 3.2-25)

Examine the solution for very fast reactions, i.e.,

$\boxed{\alpha \longrightarrow \infty}$ with $\frac{\beta}{\alpha}$ = constant

(which leaves K to be constant

$\Rightarrow \tanh x \to 1$

$\cosh x - \sinh x \to e^{-x}$

$$\Rightarrow \boxed{\Theta_A(\eta) = \left[\frac{\mu + (\beta/\alpha)}{1+(\beta/\alpha)}\right] + \left[\frac{1-\mu}{1+(\beta/\alpha)}\right] e^{-\eta\sqrt{\alpha+\beta}}}$$

and equivalent eq. for $\Theta_B(\eta)$

Example 3.2-2 : Reversible Homogeneous Reaction in a Liquid

$$\eta = \frac{y}{L}, \qquad \theta_A = \frac{C_A}{C_{A0}}, \qquad \theta_B = \frac{KC_B}{C_{A0}}. \tag{3.2-20}$$

The dimensionless concentrations have been chosen so that $\theta_A = \theta_B$ at equilibrium. After changing variables and eliminating C_B as described above, Eq. (3.2-12) and its boundary conditions become[2]

Conservation Governing Eq. (dimensionless)

$$\boxed{\frac{d^2\theta_A}{d\eta^2} = (\alpha+\beta)\theta_A - (\alpha\gamma+\beta)} \tag{3.2-21}$$

BCs

$$\theta_A(0) = 1, \qquad \frac{d\theta_A}{d\eta}(1) = 0. \tag{3.2-22}$$

The dimensionless parameters that appear are

Damköhler α, β

$$\alpha = \frac{k_1 L^2}{D_A}, \qquad \beta = \frac{k_{-1} L^2}{D_B}, \qquad \gamma = \frac{KC_{B0}}{C_{A0}}. \tag{3.2-23}$$

Plots of Eqs. (3.2-24) and (3.2-25) for moderate and fast reactions (with γ=0) are shown in Fig. 3-4. For $\alpha = \beta = 1$ the reaction $A \to B$ proceeds at significant rates throughout the film, whereas for $\alpha = \beta = 100$ there are distinct reaction and equilibrium zones, as discussed above.

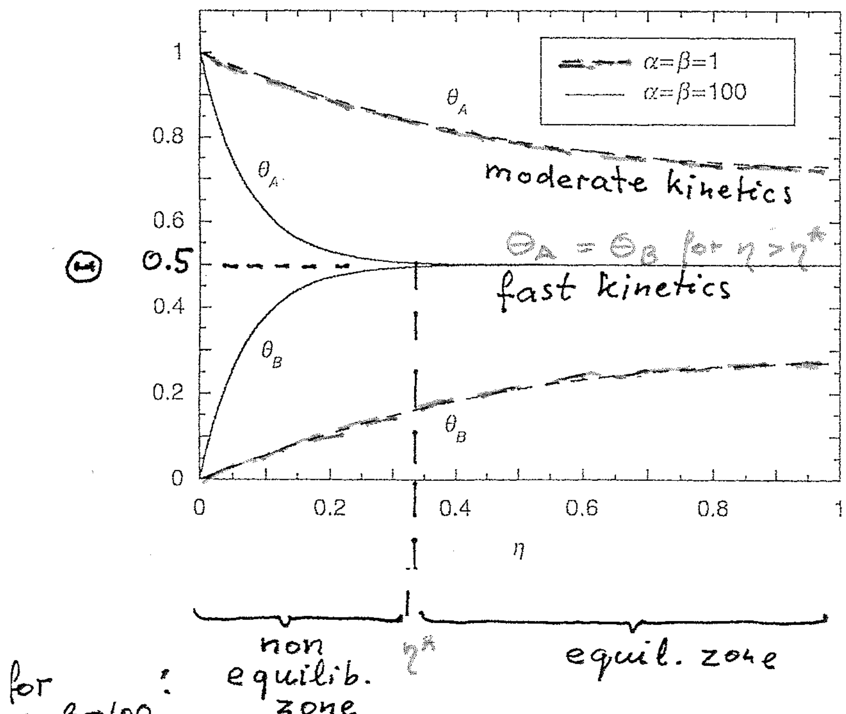

Fig. 3-4 Reactant concentrations for steady diffusion in a liquid film with a reversible homogeneous reaction, Example 3.2-2. Results from Eqs. (3.2-24) and (3.2-25) are shown for moderate ($\alpha = \beta = 1$) (and $\alpha = \beta = 100$) reaction kinetics. In both cases it is assumed that $\gamma = 0$.

The solution to Eq. (3.2-21) is

$$\theta_A(\eta) = \left[\frac{\alpha\gamma+\beta}{\alpha+\beta}\right] + \left[\frac{\alpha(1-\gamma)}{\alpha+\beta}\right]\left[\cosh\left(\eta\sqrt{\alpha+\beta}\right) - \tanh\left(\sqrt{\alpha+\beta}\right)\sinh\left(\eta\sqrt{\alpha+\beta}\right)\right]. \tag{3.2-24}$$

As in Example 3.2-1, the finite film thickness motivates the use of hyperbolic functions rather than exponentials. The corresponding result for species B is

$$\theta_B(\eta) = \left[\frac{\alpha\gamma+\beta}{\alpha+\beta}\right] - \left[\frac{\beta(1-\gamma)}{\alpha+\beta}\right]\left[\cosh\left(\eta\sqrt{\alpha+\beta}\right) - \tanh\left(\sqrt{\alpha+\beta}\right)\sinh\left(\eta\sqrt{\alpha+\beta}\right)\right]. \tag{3.2-25}$$

These results are exact for all values of the three parameters.

Approx: Very fast reaction $\alpha \to \infty$

$$\theta_A(\eta) = \left[\frac{\gamma+(\beta/\alpha)}{1+(\beta/\alpha)}\right] + \left[\frac{1-\gamma}{1+(\beta/\alpha)}\right]e^{-\eta\sqrt{\alpha+\beta}} \tag{3.2-26}$$

$$\theta_B(\eta) = \left[\frac{\gamma+(\beta/\alpha)}{1+(\beta/\alpha)}\right] - \left[\frac{(\beta/\alpha)(1-\gamma)}{1+(\beta/\alpha)}\right]e^{-\eta\sqrt{\alpha+\beta}}. \tag{3.2-27}$$

Over most of the film (except near $\eta = 0$) the exponential terms will be negligible, so that

$$\theta_A \cong \left[\frac{\gamma+(\beta/\alpha)}{1+(\beta/\alpha)}\right] \cong \theta_B. \quad \text{for } \eta > \eta^* \tag{3.2-28}$$

fast kinetics