Boundary layer mass transfer & surface reaction

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For a first-order reaction, for example, the reactant flux in the positive y-direction is equal to the flux due to reaction of component *A* at the surface,

$$J_A = -k\, C_{tot}\, \omega_A(0)$$

The reactant flux is also equal to the diffusive flux of A in the positive y-direction from the surface into the fluid,

$$J_A = C_{tot} D_{AB} \left[-\frac{\partial \omega_A}{\partial y} \right]_{y=0}$$

where C_{tot} is the total molar concentration of the fluid and ω_A is the mole fraction of reactant *A*.

These equations and the boundary layer velocity solution hold only for equimolar counter-diffusion, i.e., for a surface reaction in which the number of moles of gas-phase reactants equal the number of moles of gas-phase products. For other reactions, this solution can be approached closely for reactants which are dilute in an inert gas.

We can get the gradient in mole fraction at the surface from the boundary layer solution.

$$\left[\frac{\partial \omega_A}{\partial y} \right]_{y=0} = [\omega_A(\infty) - \omega(0)] \left[\frac{\partial \theta_A}{\partial y} \right]_{y=0}$$

$$\theta = \frac{\omega_A - \omega_A(0)}{\omega_A(\infty) - \omega_A(0)}$$

$$\frac{\partial \theta}{\partial y} = \frac{\partial \theta}{\partial \eta} \frac{\partial \eta}{\partial y} = \theta' \frac{\partial \eta}{\partial y}$$

$$\eta = \frac{y}{2} \sqrt{\frac{U}{\nu x}}$$

$$\frac{\partial \eta}{\partial y} = \frac{1}{2} \sqrt{\frac{U}{\nu x}}$$

$$\left[\frac{\partial \theta}{\partial y} \right]_{y=0} = \frac{1}{2} \sqrt{\frac{U}{\nu x}} [\theta']_{\eta=0}$$

For $\Lambda = Sc = (\nu / D_{AB}) = 1$ which is a reasonable *Sc* for gases at ambient conditions, $[\theta']_{\eta=0} = 0.664 \approx 2/3$. For other *Sc*, $[\theta']_{\eta=0} \approx (2/3)\, Sc^{1/3}$. We get, for *Sc* = 1,

$$\left[\frac{\partial \omega_A}{\partial y}\right]_{y=0} = [\omega_A(\infty) - \omega_A(0)]\frac{1}{3}\sqrt{\frac{U}{\nu x}}$$

So now we have the diffusive flux at the surface,

$$J_A = -[\omega_A(\infty) - \omega_A(0)]\frac{C_{tot} D_{AB}}{3}\sqrt{\frac{U}{\nu x}}$$

Setting this equal to the surface reaction rate expression, we can solve for the flux at the surface due to reaction that is coupled to mass transport in the boundary layer:

$$J_A = -\left[\frac{\frac{D_{AB}}{3}\sqrt{\frac{U}{\nu x}}}{1 + \frac{D_{AB}}{3}\sqrt{\frac{U}{\nu x}}}\right] k\, C_{tot}\, \omega_A(\infty)$$

Perhaps we can think of this group as an "effectiveness factor" for this first-order reaction and boundary layer flow:

$$\left[\frac{\frac{D_{AB}}{3}\sqrt{\frac{U}{\nu x}}}{1 + \frac{D_{AB}}{3}\sqrt{\frac{U}{\nu x}}}\right]$$

For

$$\left[\frac{D_{AB}}{3}\sqrt{\frac{U}{\nu x}}\right] \rightarrow \infty$$

$$J_A \rightarrow -k\, C_{tot}\, \omega_A(\infty)$$

as expected. Remember that the coefficient value of (1/3) here is approximate for the case of $Sc = \nu / D_{AB} = 1$.

For other Sc,

$$\left[\frac{\frac{D_{AB} Sc^{1/3}}{3}\sqrt{\frac{U}{\nu x}}}{1 + \frac{D_{AB} Sc^{1/3}}{3}\sqrt{\frac{U}{\nu x}}}\right] = \left[\frac{\frac{D_{AB}^{2/3}}{3\nu^{1/6}}\sqrt{\frac{U}{x}}}{1 + \frac{D_{AB}^{2/3}}{3\nu^{1/6}}\sqrt{\frac{U}{x}}}\right]$$

Note that the reactive flux at the surface - the solid film deposition rate for CVD - will decrease with increasing x-position.

How can we make the reaction rate more uniform with x-position? One way is to put the wafer downstream of the leading edge of the susceptor. Another way is to tilt the wafer a little to face the fluid flow in order to add a u_y velocity component toward the surface ($u_y < 0$).

Mass transfer film thickness δ_c

You will hear about mass transfer "film thickness," or mass transfer "boundary layer thickness." You may hear this used as if there is a stagnant fluid boundary layer instead of the actual flowing boundary layer. In reality, the velocity profile is roughly linear over the velocity boundary layer, changing from zero velocity at the surface to the free-stream velocity.

Let us look at the definition of the film thickness δ_c.

$$\delta_c \equiv \frac{\omega_A(\infty)-\omega_A(0)}{\left[\partial \omega_A / \partial y\right]_{y=0}} \quad \text{and, so} \quad \left[\frac{\partial \omega_A}{\partial y}\right]_{y=0} = \left[\frac{\omega_A(\infty)-\omega_A(0)}{\delta_c}\right]$$

Such that

$$J_A = C_{tot} D_{AB}\left[-\frac{\partial \omega_A}{\partial y}\right]_{y=0} = C_{tot} D_{AB}\left[-\frac{\omega_A(\infty)-\omega_A(0)}{\delta_c}\right]$$

$$\left[\frac{\partial \omega_A}{\partial y}\right]_{y=0} = [\omega_A(\infty)-\omega_A(0)]\left[\frac{\partial \theta}{\partial y}\right]_{y=0} \quad \text{from above}$$

$$\left[\frac{\partial \theta}{\partial y}\right]_{y=0} = \frac{1}{2}\sqrt{\frac{U}{x\nu}}[\theta']_{\eta=0} \quad \text{from above}$$

$$\delta_c = \frac{\omega_A(\infty)-\omega_A(0)}{\left[\partial \omega_A / \partial y\right]_{y=0}} = \frac{\omega_A(\infty)-\omega_A(0)}{[\omega_A(\infty)-\omega_A(0)]\frac{1}{2}\sqrt{\frac{U}{x\nu}}[\theta']_{\eta=0}}$$

$$\delta_c = 2\sqrt{\frac{x\nu}{U}}\left(\frac{1}{(2/3)\,Sc^{1/3}}\right)$$

$$\delta_c = 3\sqrt{\frac{x\nu}{U}}\,Sc^{-1/3}$$

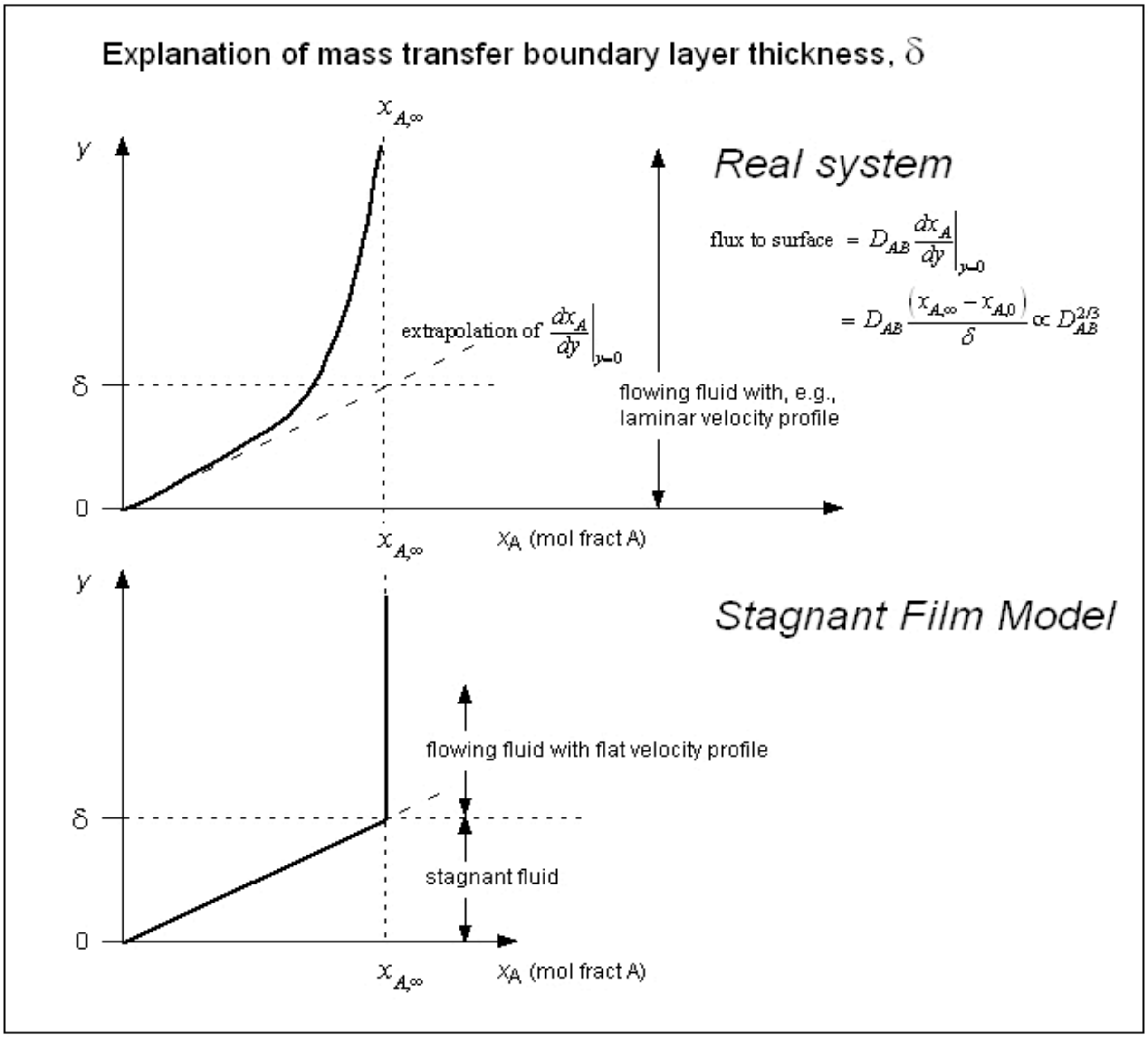
The concentration boundary layer thickness, δ_c, relative to the velocity boundary layer thickness, δ_v (distance from surface at which u_x/U = 0.99), is inversely proportional to the cube root of the Schmidt number and, thus, proportional to the cube root of the mass diffusivity.

$$\frac{\delta_c}{\delta_v} \propto \frac{1}{Sc^{1/3}} = \left(\frac{D_{AB}}{\nu}\right)^{1/3} \quad \text{where} \quad Sc = \frac{\nu}{D_{AB}} = \frac{\textit{momentum diffusion}}{\textit{mass diffusion}} \quad \text{and where} \quad \nu = \frac{\mu}{\rho}$$

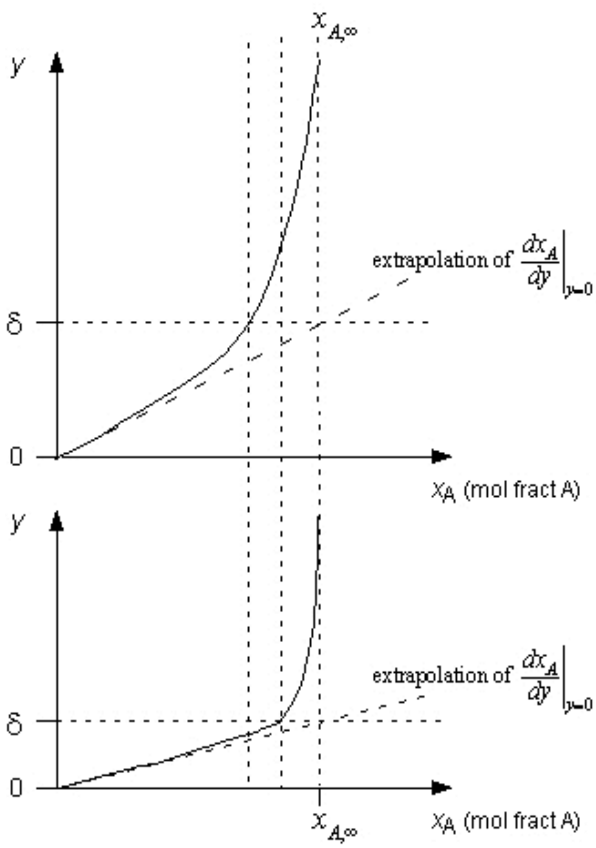
The temperature boundary layer thickness, δ_t, relative to the velocity boundary layer thickness is inversely proportional to the cube root of the Prandtl number and, thus, proportional to the cube root of the thermal diffusivity.

$$\frac{\delta_t}{\delta_v} \propto \frac{1}{Pr^{1/3}} = \left(\frac{\alpha}{\nu}\right)^{1/3} \quad \text{where} \quad Pr = \frac{\nu}{\alpha} = \frac{\textit{momentum diffusion}}{\textit{thermal diffusion}} \quad \text{and where} \quad \alpha = \frac{k_t}{\rho C_p}$$

NOTE: In the figures below, mole fraction is x_A



Changes in mass transfer boundary layer thickness and flux with change in diffusivity



The top plot has:

- larger D_{AB} thus smaller Sc
- larger δ
- at δ, smaller approach to $x_{A,\infty}$
- larger flux to surface

$$\delta \propto Sc^{-1/3} \propto D_{AB}{}^{1/3}$$

$$\left.\frac{dx_A}{dy}\right|_{y=0} \propto \frac{1}{\delta} \propto \frac{1}{D_{AB}^{1/3}}$$

$$\text{flux to surface } = D_{AB}\left.\frac{dx_A}{dy}\right|_{y=0} = D_{AB}\frac{\left(x_{A,\infty} - x_{A,0}\right)}{\delta} \propto D_{AB}^{2/3}$$