

# Mass Transfer

transport of one constituent from a region of higher concentration to that of a lower concentration

**Table 24.1** Concentrations in a binary mixture of *A* and *B*

Mass concentrations	
$\rho$ = total mass density of the mixture	
$\rho_A$ = mass density of species <i>A</i>	
$\rho_B$ = mass density of species <i>B</i>	
$\omega_A$ = mass fraction of species <i>A</i> = $\rho_A/\rho$	
$\omega_B$ = mass fraction of species <i>B</i> = $\rho_B/\rho$	
$\rho = \rho_A + \rho_B$	
$1 = \omega_A + \omega_B$	
Molar concentrations	
<i>Liquid or solid mixture</i>	<i>Gas mixture</i>
$c$ = molar density of mixture = $n/V$	$c = n/V = P/RT$
$c_A$ = molar density of species <i>A</i> = $n_A/V$	$c_A = n_A/V = p_A/RT$
$c_B$ = molar density of species <i>B</i> = $n_B/V$	$c_B = n_B/V = p_B/RT$
$x_A$ = mole fraction of species <i>A</i> = $c_A/c = n_A/n$	$y_A = c_A/c = n_A/n = p_A/p$
$x_B$ = mole fraction of species <i>B</i> = $c_B/c = n_B/n$	$y_B = c_B/c = n_B/n = p_B/p$
$c = c_A + c_B$	$c = c_A + c_B = \frac{p_A}{RT} + \frac{p_B}{RT} = \frac{P}{RT}$
$1 = x_A + x_B$	$1 = y_A + y_B$
Interrelations	
$x_A$ or	$\rho_A = c_A M_A$ $y_A = \frac{\omega_A/M_A}{\omega_A/M_A + \omega_B/M_B}$ (24-10)
	$\omega_A = \frac{x_A M_A}{x_A M_A + x_B M_B}$ or $\frac{y_A M_A}{y_A M_A + y_B M_B}$ (24-11)

mass average velocity

$$v = \frac{\sum_{i=1}^n \rho_i v_i}{\sum_{i=1}^n \rho_i} = \frac{\sum_{i=1}^n \rho_i v_i}{\rho}$$

absolute velocity of species  $i$  relative to stationary coordinate axis

molar average velocity

$$V = \frac{\sum_{i=1}^n c_i v_i}{\sum_{i=1}^n c_i} = \frac{\sum_{i=1}^n c_i v_i}{c}$$

molar flux relative to the molar average velocity

$$J_{A,z} = -D_{AB} \frac{dc_A}{dz}$$

mass flux relative to the molar average velocity

$$j_{A,z} = -D_{AB} \frac{d\rho_A}{dz}$$

molar flux relative to a set of stationary axes

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z})$$

mass flux relative to a set of stationary axes

$$n_A = -D_{AB} \nabla \rho_A + \omega_A (n_A + n_B)$$

for multicomponent mixture

$$N_A = -cD_{AM} \nabla y_A + y_A \sum_{i=1}^n N_i$$

concentration gradient contribution      bulk motion contribution

**Table 24.2** Equivalent forms of the mass flux equation for binary system *A* and *B*

Flux	Gradient	Fick rate equation	Restrictions
$\mathbf{n}_A$	$\nabla\omega_A$	$\mathbf{n}_A = -\rho D_{AB} \nabla\omega_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	Constant $\rho$
	$\nabla\rho_A$	$\mathbf{n}_A = -D_{AB} \nabla\rho_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	
$\mathbf{N}_A$	$\nabla y_A$	$\mathbf{N}_A = -c D_{AB} \nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	Constant $c$
	$\nabla c_A$	$\mathbf{N}_A = -D_{AB} \nabla c_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	
$\mathbf{j}_A$	$\nabla\omega_A$	$\mathbf{j}_A = -\rho D_{AB} \nabla\omega_A$	Constant $\rho$
	$\nabla\rho_A$	$\mathbf{j}_A = -D_{AB} \nabla\rho_A$	
$\mathbf{j}_A$	$\nabla y_A$	$\mathbf{J}_A = -c D_{AB} \nabla y_A$	Constant $c$
	$\nabla c_A$	$\mathbf{J}_A = -D_{AB} \nabla c_A$	

convective mass transfer

$$N_A = k_c \Delta c_A$$

molar mass transfer relative to fixed spacial coordinates

convective mass transfer coeff.

concentration difference between the boundary surface conc and the average conc of the fluid stream

## Differential equation for mass transfer

equation of continuity for component A  $\nabla \cdot \mathbf{n}_A + \frac{\partial \rho_A}{\partial t} - \underline{r_A} = 0$

equation of continuity for the mixture  $\nabla \cdot \rho \mathbf{v} + \frac{\partial \rho}{\partial t} = 0$  rate of mass production

in terms of molar units

equation of continuity for component A  $\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - \underline{R_A} = 0$  rate of molar production

equation of continuity for the mixture  $\nabla \cdot c \mathbf{V} + \frac{\partial c}{\partial t} - \underline{(R_A + R_B)} = 0$

depends on stoichiometry

if density is constant,

$$\mathbf{v} \cdot \nabla c_A + \frac{\partial c_A}{\partial t} = D_{AB} \nabla^2 c_A + R_A$$

$$\frac{\partial c_A}{\partial t} = D_{AB} \left[ \frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} \right]$$

$$\frac{\partial c_A}{\partial t} = D_{AB} \left[ \frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2} \right]$$

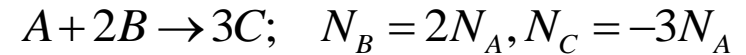
## Boundary conditions

### 1. Concentration at a boundary surface is specified

- A pure component in one phase and a mixture in the second phase, the concentration is at thermodynamic saturation conditions
- For a gas mixture in contact with a pure volatile liquid or solid A, the partial pressure of A in the gas at the surface is saturation vapor pressure
- For a liquid mixture in contact with a pure solid A, the concentration of A in the liquid at the surface is the solubility limit of A in the liquid
- For a contacting gas and liquid, if both species in the liquid phase are volatile, the boundary condition at the gas-liquid surface is defined by Raoult's law  $p_{As} = x_A P_A$
- For solutions where species A is only weakly soluble in the liquid, Henry's law may be used  $p_A = H \cdot x_A$

## Boundary conditions

2. A reacting surface boundary is specified



- The flux of one species may be related to the flux of another species by chemical reaction stoichiometry

- A finite rate of chemical reaction might exist at the surface

- The reaction may be so rapid that  $C_{As}=0$

$$N_A|_z = -k_c c_{As}$$

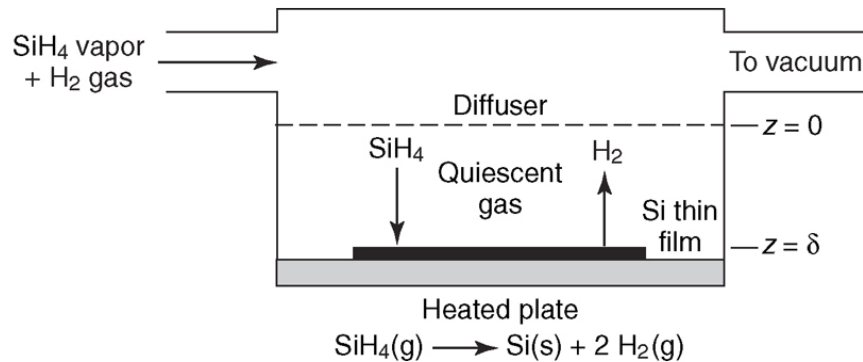
3. The flux is zero at a boundary or at a centerline of symmetry

$$N_A|_{z=0} = -D_{AB} \frac{\partial c_A}{\partial z} \Big|_{z=0} = 0 \quad \text{or} \quad \frac{\partial c_A}{\partial z} \Big|_{z=0} = 0$$

4. The convective mass transfer flux at the boundary surface is specified

$$N_A|_{z=0} = k_c (c_{As} - c_{A\infty})$$

## Fabrication of silicon wafer by CVD



A1; rxn occurs only at the surface of growing Si thin film

-> no homogeneous rxn

A2; gas phase is not externally mixed

-> molecular diffusion dominates

A3; feed gas provides silane in high excess

-> silane conc at boundary is constant

A4; flux is 1-dimensional

A5; thickness of Si film is very thin

-> diffusion path length ( $\delta$ ) is constant

A6; mass transfer process within diffusion zone is at steady state



$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} + \frac{\partial c_A}{\partial t} - R_A = 0$$

$$\frac{dN_{A,z}}{dz} = 0$$

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z})$$

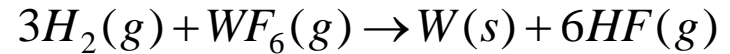
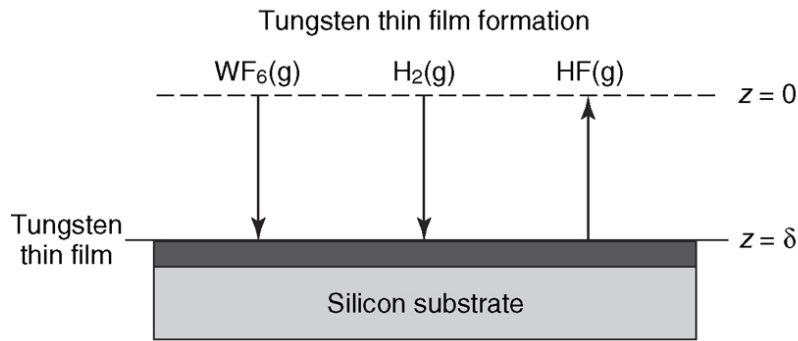
$$\frac{N_{A,z}}{N_{B,z}} = \frac{-1 \text{ mol SiH}_4 \text{ reacted}}{+2 \text{ mol H}_2 \text{ formed}} = -\frac{1}{2}$$

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} - 2N_{A,z}) = -\frac{cD_{AB}}{1 + y_A} \frac{dy_A}{dz}$$

$$N_{A,z} \int_0^\delta dz = -\int_{y_{A0}}^{y_{As}} \frac{cD_{AB}}{1 + y_A} dy_A$$

$$N_{A,z} = \frac{cD_{AB}}{\delta} \ln \left( \frac{1 + y_{A0}}{1 + y_{As}} \right)$$

# formation of a tungsten thin film on a silicon wafer by CVD



$$N_{A,z} = -cD_{A-mix} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z} + N_{C,z})$$

$$\frac{N_{A,z}}{N_{B,z}} = \frac{-1 \text{ mol } WF_6 \text{ reacted}}{-3 \text{ mol } H_2 \text{ reacted}} = \frac{1}{3} \qquad \frac{N_{A,z}}{N_{C,z}} = \frac{-1 \text{ mol } WF_6 \text{ reacted}}{+6 \text{ mol } HF \text{ formed}} = -\frac{1}{6}$$

$$N_{A,z} = -cD_{A-mix} \frac{dy_A}{dz} + y_A (N_{A,z} + 3N_{A,z} - 6N_{A,z})$$

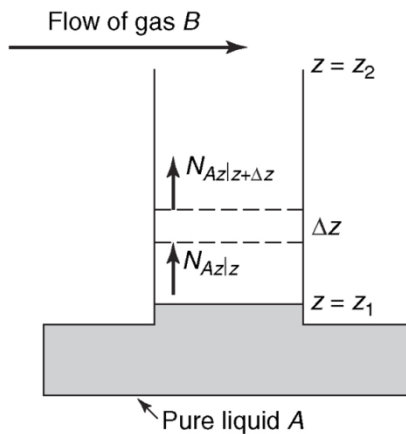
$$N_{A,z} = -\frac{cD_{A-mix}}{1 + 2y_A} \frac{dy_A}{dz}$$

## steady state molecular diffusion (1-D, no chemical rxn)

$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z})$$

### unimolecular diffusion



A vaporizes and diffuses into the gas phase  
 Gas B has a negligible solubility in liquid A,  
 and is chemically inert to A

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} + \frac{\partial c_A}{\partial t} - R_A = 0$$

$$\frac{dN_{A,z}}{dz} = 0 \quad \frac{d}{dz} N_{B,z} = 0$$

$N_{B,z}$  at  $z=z_1$  is zero  $\rightarrow N_{B,z}$  (net flux of B) is zero

$$N_{A,z} = -\frac{cD_{AB}}{1-y_A} \frac{dy_A}{dz}$$

$\rightarrow$  B is a stagnant gas

$$N_{A,z} = -\frac{cD_{AB}}{1-y_A} \frac{dy_A}{dz} \quad z = z_1 \quad y_A = y_{A_1} \quad z = z_2 \quad y_A = y_{A_2}$$

$$N_{A,z} \int_{z_1}^{z_2} dz = cD_{AB} \int_{y_{A_1}}^{y_{A_2}} -\frac{dy_A}{1-y_A} \quad N_{A,z} = \frac{cD_{AB}}{(z_2 - z_1)} \ln \frac{(1-y_{A_2})}{(1-y_{A_1})}$$

$$y_{B,lm} = \frac{y_{B_2} - y_{B_1}}{\ln(y_{B_2} / y_{B_1})} \quad y_{B,lm} = \frac{(1-y_{A_2}) - (1-y_{A_1})}{\ln \left[ \frac{(1-y_{A_2})}{(1-y_{A_1})} \right]} = \frac{y_{A_1} - y_{A_2}}{\ln \left[ \frac{(1-y_{A_2})}{(1-y_{A_1})} \right]}$$

$$N_{A,z} = \frac{cD_{AB}}{z_2 - z_1} \frac{(y_{A_1} - y_{A_2})}{y_{B,lm}}$$

For an ideal gas,  $c = \frac{n}{V} = \frac{P}{RT} \quad y_A = \frac{p_A}{P}$

$$N_{A,z} = \frac{D_{AB}P}{RT(z_2 - z_1)} \frac{(p_{A_1} - p_{A_2})}{p_{B,lm}}$$

Steady state diffusion of one gas through a second stagnant gas;  
Absorption, humidification

$$\frac{dN_{A,z}}{dz} = 0 \quad N_{A,z} = -\frac{cD_{AB}}{1-y_A} \frac{dy_A}{dz} \quad \frac{d}{dz} \left( -\frac{cD_{AB}}{1-y_A} \frac{dy_A}{dz} \right) = 0 \quad \frac{d}{dz} \left( \frac{1}{1-y_A} \frac{dy_A}{dz} \right) = 0$$

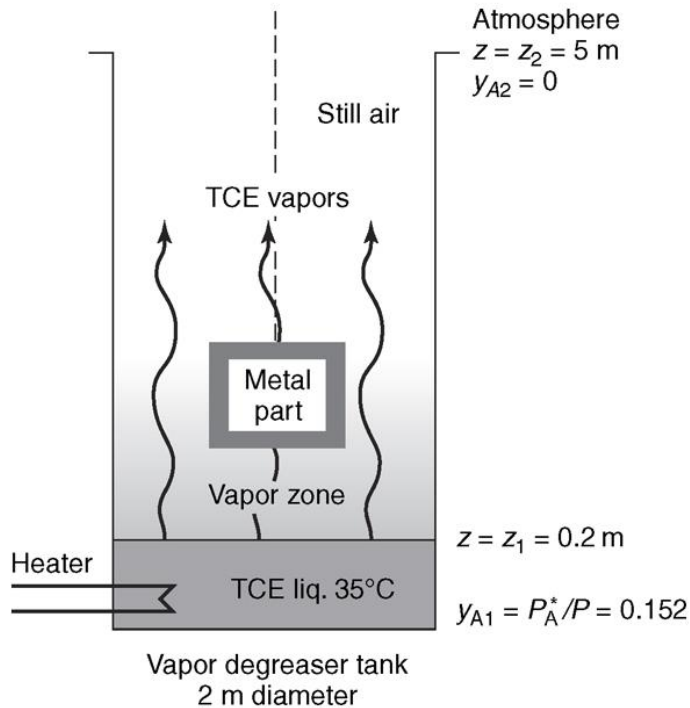
$$-\ln(1-y_A) = c_1 z + c_2 \quad z = z_1 \quad y_A = y_{A_1} \quad z = z_2 \quad y_A = y_{A_2}$$

$$\left( \frac{1-y_A}{1-y_{A_1}} \right) = \left( \frac{1-y_{A_2}}{1-y_{A_1}} \right)^{(z-z_1)/(z_2-z_1)} \quad \left( \frac{y_B}{y_{B_1}} \right) = \left( \frac{y_{B_2}}{y_{B_1}} \right)^{(z-z_1)/(z_2-z_1)}$$

average concentration of one of the species along the diffusion path

$$\begin{aligned} \bar{y}_B &= \frac{\int_{z_1}^{z_2} y_B dz}{\int_{z_1}^{z_2} dz} \\ \bar{y}_B &= y_{B_1} \frac{\int_{z_1}^{z_2} \left( \frac{y_{B_2}}{y_{B_1}} \right)^{(z-z_1)/(z_2-z_1)} dz}{z_2 - z_1} \\ &= \frac{(y_{B_2} - y_{B_1})(z_2 - z_1)}{\ln(y_{B_2} / y_{B_1})(z_2 - z_1)} = \frac{y_{B_2} - y_{B_1}}{\ln(y_{B_2} / y_{B_1})} \\ &= y_{B,lm} \end{aligned}$$

## Vapor degreaser; cleaning metal parts



regulation; greaser cannot emit more than 1.0 kg TCE per day

$M_w = 131.4 \text{ g/mol}$

vapor pressure = 115.5 mmHg

$D_{AB} = 0.088 \text{ cm}^2/\text{s}$

$$c = \frac{P}{RT} = \frac{1}{(0.082)(273 + 35)} = 0.0396 \frac{\text{kg mol}}{\text{m}^3}$$

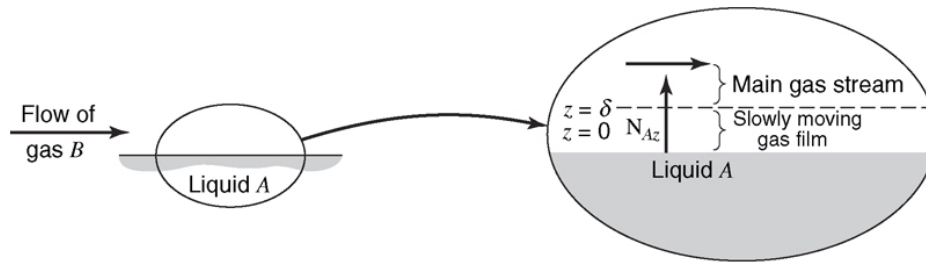
$$y_{A1} = \frac{P_A}{P} = \frac{115.5 \text{ mmHg}}{1 \text{ atm}} \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.152$$

$$N_{A,z} = \frac{cD_{AB}}{(z_2 - z_1)} \ln \frac{(1 - y_{A2})}{(1 - y_{A1})}$$

$$N_{A,z} = \frac{(0.0396)(0.088 \times 10^{-4})}{(5.0 - 0.2)} \ln \frac{(1 - 0)}{(1 - 0.152)} = 1.197 \times 10^{-8}$$

$$W_A = N_{A,z} \frac{\pi D^2}{4} = 0.423 \frac{\text{kg TCE}}{\text{day}}$$

## film theory

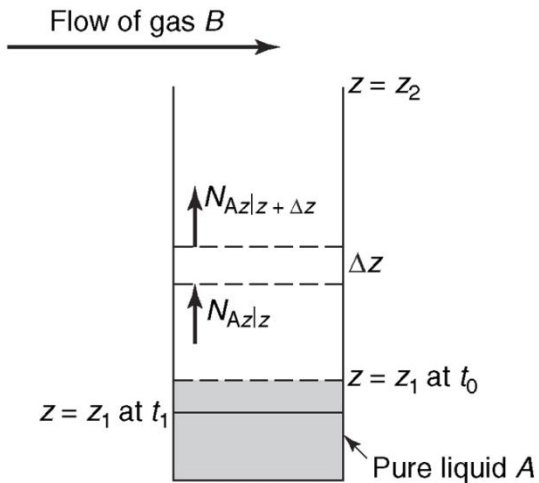


$$N_{A,z} = \frac{D_{AB}P}{RT(z_2 - z_1)} \frac{(p_{A_1} - p_{A_2})}{p_{B,lm}}$$

$$N_{A,z} = \frac{D_{AB}P}{RT p_{B,lm} \delta} (p_{A_1} - p_{A_2}) \quad N_{A,z} = k_c (c_{A_1} - c_{A_2}) = \frac{k_c}{RT} (p_{A_1} - p_{A_2}) \quad k_c = \frac{D_{AB}P}{p_{B,lm} \delta}$$

$k_c$  is a function of the diffusion coefficient raised to an exponent varying from 0.5 to 1.0

## pseudo-steady-state diffusion



when the length of the diffusion path changes a small amount over a long period of time

$$N_{A,z} = \frac{cD_{AB}}{z_2 - z_1} \frac{(y_{A_1} - y_{A_2})}{y_{B,lm}}$$

$$N_{A,z} = \frac{cD_{AB}(y_{A_1} - y_{A_2})}{zy_{B,lm}}$$

$$N_{A,z} = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt}$$

$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{cD_{AB}(y_{A_1} - y_{A_2})}{zy_{B,lm}}$$

molar density of A  
in the liquid phase

$$\int_{t=0}^t dt = \frac{\rho_{A,L} y_{B,lm} / M_A}{cD_{AB}(y_{A_1} - y_{A_2})} \int_{z_{t_0}}^{z_t} z \, dz$$

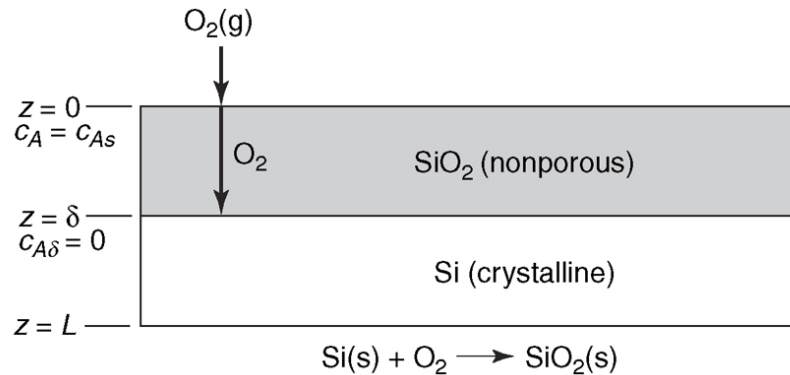
$$t = \frac{\rho_{A,L} y_{B,lm} / M_A}{cD_{AB}(y_{A_1} - y_{A_2})} \left( \frac{z_t^2 - z_{t_0}^2}{2} \right)$$

$$D_{AB} = \frac{\rho_{A,L} y_{B,lm} / M_A}{c(y_{A_1} - y_{A_2}) t} \left( \frac{z_t^2 - z_{t_0}^2}{2} \right)$$



## Formation of $\text{SiO}_2$ thin film on a Si wafer

- fabrication of solid state microelectronic devices



A1; oxidation of Si to  $\text{SiO}_2$  occurs only at Si/ $\text{SiO}_2$  interface

-> unreacted Si serves as the sink for molecular mass transfer of  $\text{O}_2$  through the film

A2;  $\text{O}_2$  in the gas phase represents an infinite source for  $\text{O}_2$  transfer

A3; rate of  $\text{SiO}_2$  formation is controlled by the rate of molecular diffusion of  $\text{O}_2$  through the solid  $\text{SiO}_2$  layer

A4; rxn is very rapid -> concentration of  $\text{O}_2$  at interface is zero

A5; the flux of  $\text{O}_2$  (A) through  $\text{SiO}_2$  (B) layer is 1-dimensional

A6; the rate of  $\text{SiO}_2$  film formation is slow

-> no accumulation of reactants or products within the  $\text{SiO}_2$  film

$$\frac{d}{dz} N_{A,z} = 0 \quad N_{A,z} = -D_{AB} \frac{dc_A}{dz} + \frac{c_A}{c} (N_{A,z} + N_{B,z})$$

as conc of  $O_2$  in  $SiO_2$  layer is dilute  $N_{A,z} = -D_{AB} \frac{dc_A}{dz}$

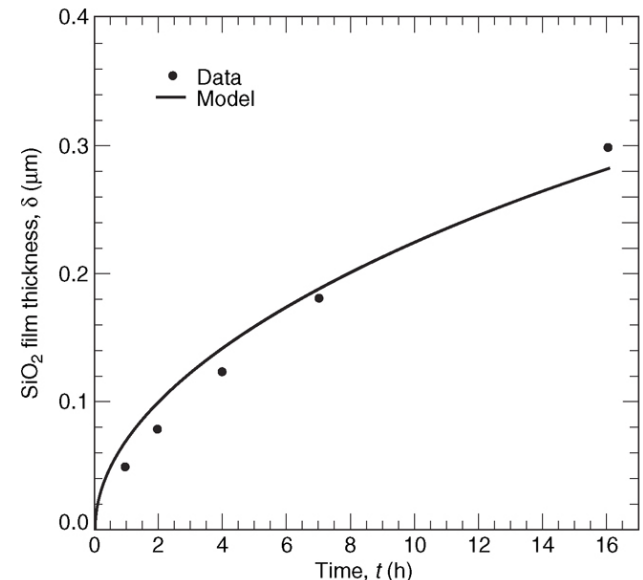
$$\int_0^{\delta} N_{A,z} dz = -D_{AB} \int_{c_{As}}^0 dc_A \quad N_{A,z} = \frac{D_{AB} c_{As}}{\delta}$$

$\delta$  increases slowly with time  $\rightarrow$  pseudo-steady-state assumption

(molar rate of  $SiO_2$  formation) = (molar rate of accumulation of  $SiO_2$ )

$$N_{A,z} S = \frac{D_{AB} c_{As}}{\delta} S \quad \frac{d\left(\frac{\rho_B S \delta}{M_B}\right)}{dt}$$

$$\int_0^{\delta} \delta d\delta = \frac{M_B D_{AB} c_{As}}{\rho_B} \int_0^t dt \quad \delta = \sqrt{\frac{2 M_B D_{AB} c_{As}}{\rho_B} t}$$



equimolar counterdiffusion

$$N_{A,z} = -N_{B,z}$$

$$N_{A,z} = -D_{AB} \frac{dc_A}{dz} + y_A (N_{A,z} + N_{B,z}) \quad N_{A,z} = -D_{AB} \frac{dc_A}{dz}$$

$$N_{A,z} \int_{z_1}^{z_2} dz = -D_{AB} \int_{c_{A_1}}^{c_{A_2}} dc_A \quad N_{A,z} = \frac{D_{AB}}{(z_2 - z_1)} (c_{A_1} - c_{A_2})$$

for ideal gas,

$$c_A = \frac{n_A}{V} = \frac{p_A}{RT}$$

$$N_{A,z} = \frac{D_{AB}}{RT(z_2 - z_1)} (p_{A_1} - p_{A_2})$$

$$\frac{d}{dz} N_{A,z} = 0 \quad \frac{d^2 c_A}{dz^2} = 0 \quad c_A = C_1 z + C_2$$

$$\frac{c_A - c_{A_1}}{c_{A_1} - c_{A_2}} = \frac{z - z_1}{z_1 - z_2}$$

## One dimensional systems with chemical reaction

homogeneous rxn; occurs uniformly throughout a given phase

heterogeneous rxn; takes place in a restricted region within or at a boundary of the phase

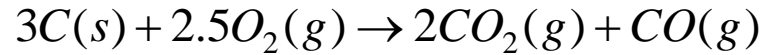
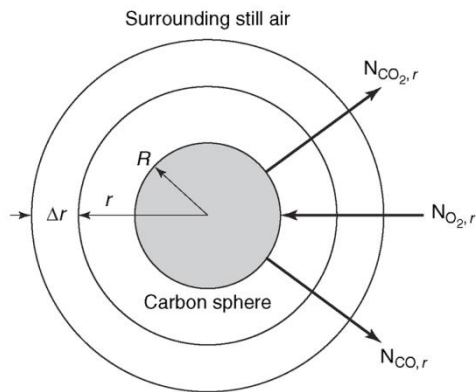
$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

only for homogenous rxn

diffusion controlled; when the rxn rate is instantaneous relative to the rate of diffusion

reaction controlled; when the rxn rate at the surface limits the mass transfer rate

## diffusion with heterogeneous 1<sup>st</sup> order chemical reaction



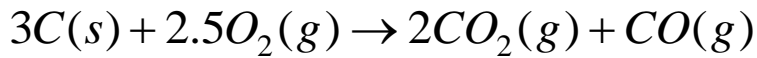
no homogeneous chemical rxn occurs along the diffusion path  $\rightarrow R_{O_2}=0$

As the coal particle is oxidized, the particle shrinks with time. It is desired to predict the size of the particle with time

diffusion controlled

$$\frac{\partial c_A}{\partial t} + \frac{1}{r^2} \frac{\partial (r^2 N_{Ar})}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (N_{A\theta} \sin \theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial N_{A\phi}}{\partial \phi} - R_A = 0 \quad \frac{1}{r^2} \frac{d(r^2 N_{Ar})}{dr} = 0$$

$$N_{O_2 r} 4\pi r^2 \Big|_r - N_{O_2 r} 4\pi r^2 \Big|_{r+\Delta r} = 0 \quad \frac{d(r^2 N_{O_2 r})}{dr} = 0 \quad r^2 N_{O_2 r} \Big|_r = R^2 N_{O_2 r} \Big|_R$$



$$N_{O_2r} = -2.5N_{CO_r} \quad \text{and} \quad N_{O_2r} = -1.25N_{CO_2r}$$

$$N_A = -cD_{AM} \nabla y_A + y_A \sum_{i=1}^n N_i$$

$$N_{O_2r} = -cD_{O_2\text{-mix}} \frac{dy_{O_2}}{dr} + y_{O_2} (N_{O_2r} + N_{CO_r} + N_{CO_2r} + N_{N_2})$$

$$N_{O_2r} = -cD_{O_2\text{-mix}} \frac{dy_{O_2}}{dr} + y_{O_2} \left( N_{O_2r} - \frac{1}{2.5} N_{O_2r} - \frac{1}{1.25} N_{O_2r} + 0 \right)$$

$$N_{O_2r} = -cD_{O_2\text{-mix}} \frac{dy_{O_2}}{dr} - 0.2y_{O_2} N_{O_2r}$$

instantaneous rxn

$$N_{O_2r} = -\frac{cD_{O_2\text{-mix}}}{1+0.2y_{O_2}} \frac{dy_{O_2}}{dr} \quad \boxed{r=R \quad y_{O_2}=0} \quad \frac{d(r^2 N_{O_2r})}{dr} = 0$$

$$r=\infty, \quad y_{O_2}=0.21$$

$$\left( r^2 N_{O_2r} \right) \int_R^\infty \frac{dr}{r^2} = -\frac{cD_{O_2\text{-mix}}}{0.2} \int_0^{0.21} \frac{0.2 dy_{O_2}}{1+0.2y_{O_2}} \quad \left( r^2 N_{O_2r} \right) \left( \frac{1}{R} \right) = \frac{cD_{O_2\text{-mix}}}{0.2} \ln \left( \frac{1}{1.042} \right)$$

the moles of oxygen transferred per time is the product of the oxygen flux and the cross sectional area

$$W_{O_2} = 4\pi r^2 N_{O_2 r} = -4\pi R \frac{cD_{O_2\text{-mix}}}{0.2} \ln(1.042)$$

negative because the direction of oxygen flux from the bulk gas to the surface is opposite to the increasing r direction from r=R to infinity

the material balance for carbon       $3C(s) + 2.5O_2(g) \rightarrow 2CO_2(g) + CO(g)$

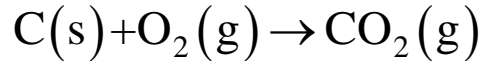
(input carbon rate) – (output carbon rate) = rate of carbon accumulation

output rate of carbon       $W_C = \frac{3}{2}W_{CO_2} = -\frac{3}{2.5}W_{O_2} = +\frac{3}{2.5}4\pi R \frac{cD_{O_2\text{-mix}}}{0.2} \ln(1.042)$

carbon accumulation rate       $\frac{\rho_C}{M_C} \frac{dV}{dt} = \frac{\rho_C}{M_C} 4\pi R^2 \frac{dR}{dt}$

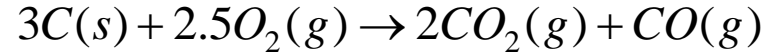
$$0 - \frac{3}{2.5}4\pi R \frac{cD_{O_2\text{-mix}}}{0.2} \ln(1.042) = \frac{\rho_C}{M_C} 4\pi R^2 \frac{dR}{dt} \qquad \theta = \frac{\frac{\rho_C}{M_C} (R_i^2 - R_f^2)}{12cD_{O_2\text{-mix}} \ln(1.042)}$$

for alternative rxn with instantaneous rxn at the surface



$$N_{O_2r} = -cD_{O_2\text{-mix}} \frac{dy_{O_2}}{dr}$$

$$W_{O_2} = -4\pi R c D_{O_2\text{-mix}} y_{O_2\infty}$$



$$N_{O_2r} = -cD_{O_2\text{-mix}} \frac{dy_{O_2}}{dr} + y_{O_2} (N_{O_2r} + N_{CO_r} + N_{CO_2r} + N_{N_2})$$

$$W_{O_2} = 4\pi r^2 N_{O_2r} = -4\pi R \frac{cD_{O_2\text{-mix}}}{0.2} \ln(1.042)$$

if the rxn is not instantaneous

$$W_{O_2} = -4\pi R c D_{O_2\text{-mix}} (y_{O_2\infty} - y_{O_2s})$$

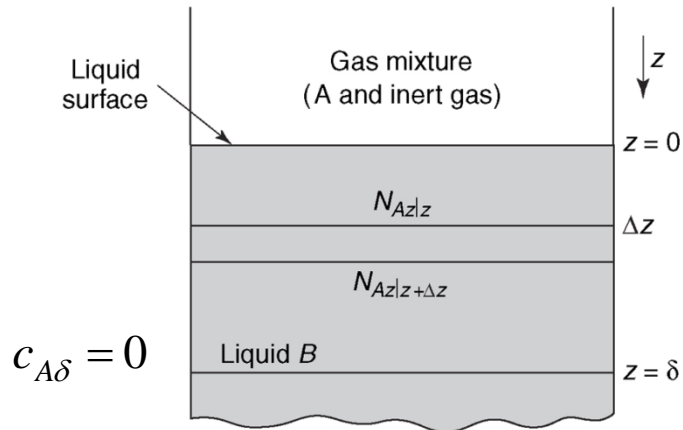
$$y_{O_2s} = \frac{c_{O_2s}}{c} = -\frac{N_{O_2R}}{k_s c} \quad W_{O_2} = -4\pi R c D_{O_2\text{-mix}} \left( y_{O_2\infty} + \frac{N_{O_2R}}{k_s c} \right) \quad N_{As} \Big|_R = -k_s c_{As}$$

$$W_{O_2} = 4\pi R^2 N_{O_2R} = 4\pi r^2 N_{O_2r} \quad R^2 N_{O_2R} \left( 1 + \frac{D_{O_2\text{-mix}}}{k_s R} \right) = -R c D_{O_2\text{-mix}} y_{O_2\infty}$$

$$W_{O_2} = -\frac{4\pi R c D_{O_2\text{-mix}} y_{O_2\infty}}{1 + \frac{D_{O_2\text{-mix}}}{k_s R}}$$



## diffusion with homogeneous 1<sup>st</sup> order chemical reaction



one of the constituents of a gas mixture is preferentially dissolved in a contacting liquid (absorption of A into B)

if there is little fluid motion and if the concentration of A is small

$$N_{A,z} = -D_{AB} \frac{dc_A}{dz} + y_A (N_{A,z} + N_{B,z}) \quad N_{A,z} = -D_{AB} \frac{dc_A}{dz}$$

$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0 \quad \frac{d}{dz} N_{A,z} - R_A = 0 \quad -R_A = k_1 c_A \quad -\frac{d}{dz} \left( D_{AB} \frac{dc_A}{dz} \right) + k_1 c_A = 0$$

$$c_A = c_1 \cosh \sqrt{k_1 / D_{AB}} z + c_2 \sinh \sqrt{k_1 / D_{AB}} z$$

$$\text{at } z=0 \quad c_A = c_{A_0}$$

$$\text{at } z=\delta \quad c_A = 0$$

$$c_A = c_{A_0} \cosh \sqrt{k_1 / D_{AB}} z - \frac{c_{A_0} \sinh \sqrt{k_1 / D_{AB}} z}{\tanh \sqrt{k_1 / D_{AB}} \delta}$$

molar mass flux at the liquid surface

$$N_{A,z} \Big|_{z=0} = \frac{D_{AB} c_{A_0}}{\delta} \left[ \frac{\sqrt{k_1 / D_{AB}} \delta}{\tanh \sqrt{k_1 / D_{AB}} \delta} \right]$$

## penetration theory

$$N_{A,z}|_{z=0} = \frac{D_{AB}c_{A_0}}{\delta} \left[ \frac{\sqrt{k_1 / D_{AB}} \delta}{\tanh \sqrt{k_1 / D_{AB}} \delta} \right]$$

as the rxn rate increases,  $N_{A,z}|_{z=0} = \sqrt{D_{AB}k_1} (c_{A_0} - 0)$        $N_{A,z} = k_c (c_{A_1} - c_{A_2})$

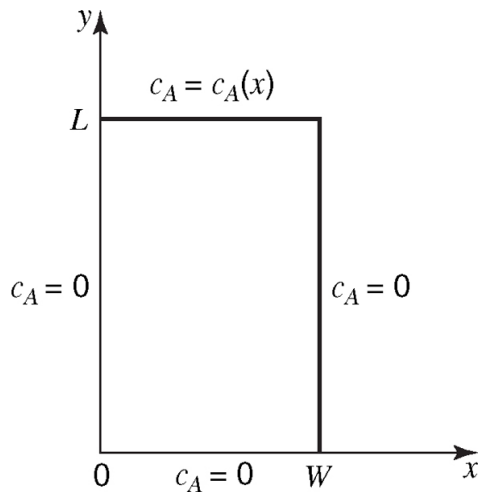
$$k_c \sim D_{AB}^{1/2}$$

film theory;  $k_c = \frac{D_{AB}P}{p_{B,lm}\delta}$        $k_c \sim D_{AB}$

boundary layer theory;  $\frac{\bar{k}_c L}{D_{AB}} = \text{Sh}_L = 0.664 \text{Re}_L^{1/2} \text{Sc}^{1/3}$        $\text{Sc} = \frac{\mu}{\rho D_{AB}}$

$$k_c \sim D_{AB}^{2/3}$$

## two- and three-dimensional systems



$$\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} = 0$$

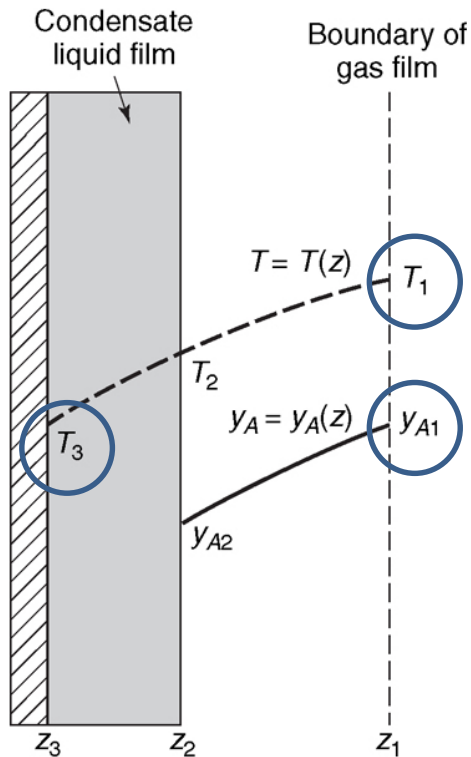
$$c_A(x, y) = X(x)Y(y)$$

$$c_A = c_A(x) = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{W} \sinh \frac{n\pi L}{W}$$

$$c_A = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{W} \sinh \frac{n\pi y}{W}$$

# simultaneous heat and mass transfer

## vapor condensation on a cold surface



$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0 \qquad \frac{d}{dz} N_{A,z} = 0$$

if A is diffusing through a stagnant gas

$$N_{A,z} = \frac{-cD_{AB}}{1-y_A} \frac{dy_A}{dz}$$

if the temperature profile is of the form

$$\frac{T}{T_1} = \left( \frac{z}{z_1} \right)^n$$

$$D_{AB} = D_{AB}|_{T_1} \left( \frac{T}{T_1} \right)^{3/2} = D_{AB}|_{T_1} \left( \frac{z}{z_1} \right)^{3n/2}$$

$$c = \frac{P}{RT} = \frac{P}{RT_1 \left( z/z_1 \right)^n}$$

$$N_{A,z} = \frac{-PD_{AB}|_{T_1}}{RT_1(1-y_A)} \left( \frac{z}{z_1} \right)^{n/2} \frac{dy_A}{dz}$$

over a small temperature range

$$N_{A,z} = -\frac{(cD_{AB})_{\text{avg}}}{(1-y_A)} \frac{dy_A}{dz} \qquad N_{A,z} = \frac{(cD_{AB})_{\text{avg}} (y_{A_1} - y_{A_2})}{(z_2 - z_1) y_{B,lm}}$$

total energy flux

$$\frac{q_z}{A} = h_{\text{liquid}} (T_2 - T_3) = h_c (T_1 - T_2) + N_{A,z} M_A (H_1 - H_2)$$

enthalpy of A  
per unit mass

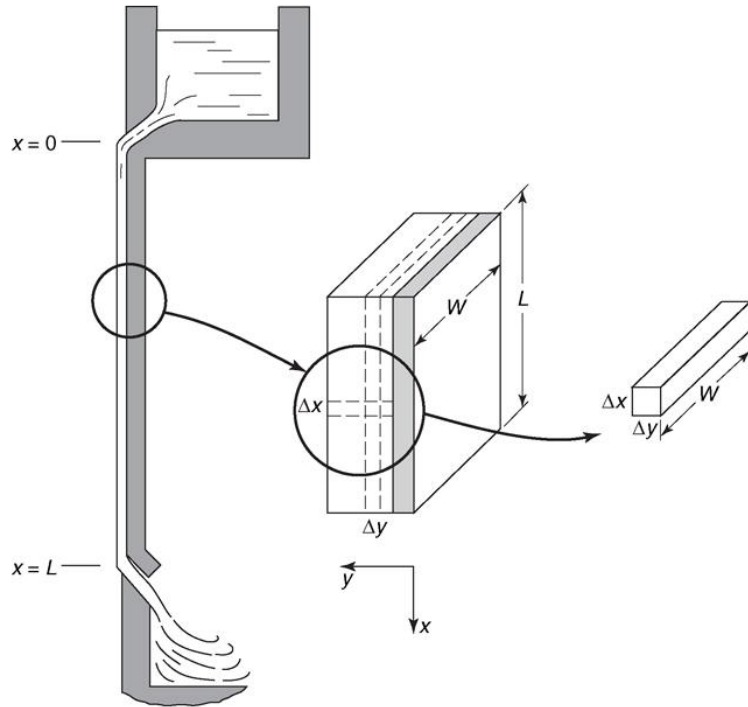
assume  $T_2$        $\text{Nu}_L = 0.68 + \frac{0.670 \text{Ra}_L^{1/4}}{\left[1 + (0.492 / \text{Pr})^{9/16}\right]^{4/9}} \quad \Rightarrow \quad h_c, (cD_{AB})_{\text{avg}}$

$$y_{A_2} = \frac{p_{A_2}}{P} \quad \text{or} \quad \frac{P_A}{P} \quad \Rightarrow \quad N_{A,z} = \frac{(cD_{AB})_{\text{avg}} (y_{A_1} - y_{A_2})}{(z_2 - z_1) y_{B,lm}}$$

check ;       $\frac{q_z}{A} = h_{\text{liquid}} (T_2 - T_3) = h_c (T_1 - T_2) + N_{A,z} M_A (H_1 - H_2)$

simultaneous momentum and mass transfer;

dissolution of one of the components  
of a gas mixture by a liquid  
time of contact is short



$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} + \frac{\partial c_A}{\partial t} - R_A = 0$$

$$\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} = 0$$

$$N_{A,x} = -D_{AB} \frac{\partial c_A}{\partial x} + x_A (N_{A,x} + N_{B,x})$$

$$N_{A,y} = -D_{AB} \frac{\partial c_A}{\partial y} + x_A (N_{A,y} + N_{B,y})$$

$$N_{A,x} = x_A (N_{A,x} + N_{B,x}) = c_A v_x$$

$$N_{A,y} = -D_{AB} \frac{\partial c_A}{\partial y}$$

$$v_x \frac{\partial c_A}{\partial x} - D_{AB} \frac{\partial^2 c_A}{\partial y^2} = 0$$

$$2v_{\max} \left[ \frac{y}{\delta} - \frac{1}{2} \left( \frac{y}{\delta} \right)^2 \right] \frac{\partial c_A}{\partial x} = D_{AB} \frac{\partial^2 c_A}{\partial y^2}$$

$$2v_{\max} \left[ \frac{y}{\delta} - \frac{1}{2} \left( \frac{y}{\delta} \right)^2 \right] \frac{\partial c_A}{\partial x} = D_{AB} \frac{\partial^2 c_A}{\partial y^2}$$

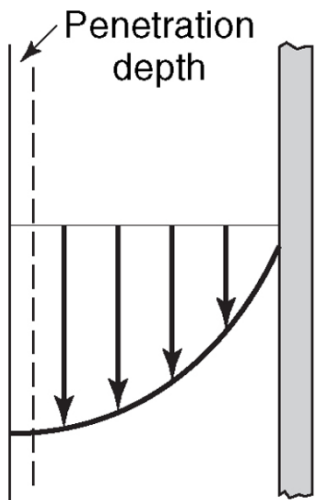
$$\frac{c_A|_{x=L} - c_A|_{y=\delta}}{c_A|_{x=0} - c_A|_{y=\delta}} = 0.7857e^{-5.1213n} + 0.1001e^{-39.318n} \\ + 0.03500e^{-105.64n} \\ + 0.01811e^{-204.75n} \\ + \dots$$

$$\text{at } x=0 \quad c_A = 0$$

$$\text{at } y=0 \quad \frac{\partial c_A}{\partial y} = 0$$

$$\text{at } y=\delta \quad c_A = c_{A_0}$$

if solute A penetrates only a short distance into the liquid film



$$v_{\max} \frac{\partial c_A}{\partial x} = D_{AB} \frac{\partial^2 c_A}{\partial y^2}$$

$$c_A(x, \xi) = c_{A0} \left[ 1 - \operatorname{erf} \left( \frac{\xi}{\sqrt{\frac{4D_{AB}x}{v_{\max}}}} \right) \right]$$

$$N_{A,y}|_{y=\delta} = c_{A0} \sqrt{\frac{D_{AB}v_{\max}}{\pi x}}$$

$$k_c = \sqrt{\frac{D_{AB}}{\pi t_{\text{exp}}}}$$

## unsteady state diffusion

### diffusion in a semi-infinite medium

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$$

$t = 0, \quad c_A(z, 0) = c_{Ao} \quad \text{for all } z$   
 $\text{at } z = 0, \quad c_A(0, t) = c_{As} \quad \text{for } t > 0$   
 $\text{at } z = \infty, \quad c_A(\infty, t) = c_{Ao} \quad \text{for all } t$

$$\frac{c_{As} - c_A}{c_{As} - c_{Ao}} = \text{erf}\left(\frac{z}{2\sqrt{D_{AB}t}}\right) \quad N_{A,z}|_{z=0} = \sqrt{\frac{D_{AB}}{\pi t}} (c_{As} - c_{Ao})$$

### diffusion in a finite-dimensional medium

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$$

$c_A = c_{Ao} \quad \text{at } t = 0 \quad \text{for } 0 \leq z \leq L$   
 $c_A = c_{As} \quad \text{at } z = 0 \quad \text{for } t > 0$   
 $c_A = c_{As} \quad \text{at } t = L \quad \text{for } t > 0$

$$\frac{c_A - c_{As}}{c_{Ao} - c_{As}} = \frac{4}{\pi} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D}, \quad n = 1, 3, 5, \dots \quad X_D = \frac{4D_{AB}t}{L^2}$$

$$N_{Az} = \frac{4D_{AB}}{L} (c_{As} - c_{Ao}) \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D}, \quad n = 1, 3, 5, \dots$$