Species balances and diffusion with reaction

1 Errata

- Slide 4 needs corrections to the title and generation term. Use the title “Continuity equation” and the volumetric generation term

$$r_A \Delta x \Delta y \Delta z$$

  The generation rate r_A has no direction subscript.

- Slide 6 mixes the reference frames for relative molar flux and convective transport. Pair $\mathbf{J}_A$ with molar-average velocity $\mathbf{v}^*$.

  Moles are conserved for any reaction with equal total stoichiometric coefficients on both sides, rather than only $\mathrm{A} \rightarrow \mathrm{B}$.

- Slide 17 places a first-order rate annotation on case 3. Move that annotation to case 4. For case 3, use constant consumption

$$R_A = -k_0$$

  The resulting concentration profile is parabolic.

- Slides 19 and 22 use inconsistent coordinates in the boundary conditions. Use x throughout

$$c_A(0) = c_{A0}, \qquad N_{Ax}(L) = 0$$

- Slide 22 gives the wrong sign for the final surface flux. Use

$$N_{Ax}(0) = c_{A0} D_{AB} m \tanh(mL)$$

  The coordinate x is directed into the liquid.

2 Reading list

- Bird et al. (2006), chapters 17 and 18.
- Geankoplis (2003), chapter 6.
- Welty et al. (2001), chapter 24.

Concentrations and molar rates use kmol unless the example states another consistent basis.

3 Locate reaction before choosing the equation

Given conditions	Model and checks
No reaction in the transfer region	Set the volume source to zero; any wall reaction appears in a boundary condition.
Finite-rate reaction at a wall	Match diffusive arrival to the surface reaction rate; retain both film and reaction resistances.
Reaction throughout the volume	Retain the local source term in the continuity equation; choose zero-order or first-order kinetics as stated.
Reaction changes total gas moles	Use stoichiometry to find all species fluxes before assuming equimolar counter-diffusion.
Flow and radial diffusion in a catalytic tube	Retain convection and the required inlet, wall and symmetry conditions.

4 Continuity equation

DEFINITION

Species continuity equation

A local species balance relating accumulation, the divergence of species flux and net production by reaction.

4.1 A fixed control volume

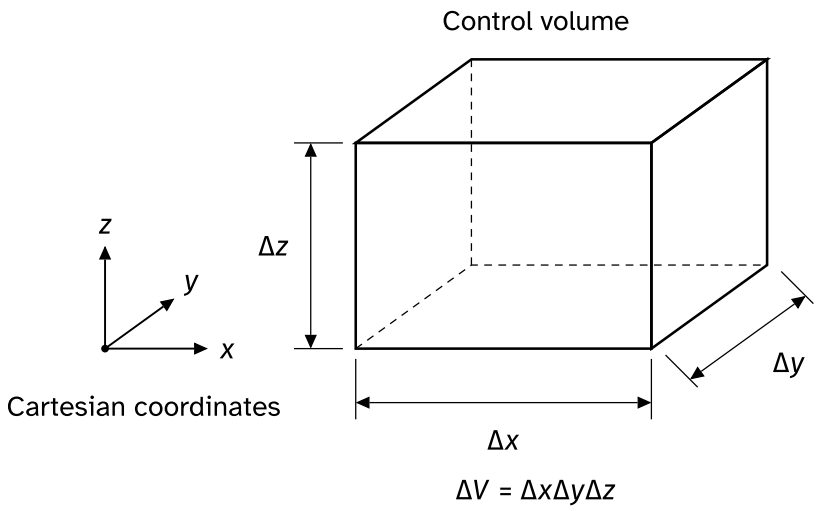


Figure 1: A fixed rectangular control volume in Cartesian coordinates, with volume $\Delta V = \Delta x\, \Delta y\, \Delta z$.

Take a stationary rectangular volume with sides Δx, Δy, Δz. Let ρ_A be the mass of A per volume, in $\mathrm{kg\,m^{-3}}$, and n_{Ax} the total mass flux of A in the positive x direction, in $\mathrm{kg\,m^{-2}\,s^{-1}}$. Production r_A is mass of A produced per volume per time, in $\mathrm{kg\,m^{-3}\,s^{-1}}$. Production has no direction subscript. The contribution of the two faces normal to x is

$$[n_{Ax}(x) - n_{Ax}(x + \Delta x)]\Delta y \Delta z$$

The balance over all faces is

$$\text{in} - \text{out} + r_A \Delta x \Delta y \Delta z = \frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z \tag{1}$$

Add the analogous y and z face contributions to Eq. 1, divide by volume, and let all three lengths approach zero. The flux difference divided by distance becomes a negative derivative. Thus

$$\begin{aligned} \frac{\partial \rho_A}{\partial t} &= -\left(\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z} \right) + r_A \\ &= -\nabla \cdot \mathbf{n}_A + r_A \end{aligned} \tag{2}$$

Every term is mass per volume per time. The minus sign means a net outward flux decreases the mass stored. Time t is in s; coordinates x, y, z are in m. Total flux already includes both convection and diffusion. In the mass-average frame, $\mathbf{n}_A = \rho_A \mathbf{v} + \mathbf{j}_A$, where velocity $\mathbf{v}$ is in m s⁻¹ and relative mass flux $\mathbf{j}_A$ in $\mathrm{kg\,m^{-2}\,s^{-1}}$. Substitution gives

$$\frac{\partial \rho_A}{\partial t} = -\nabla \cdot (\rho_A \mathbf{v}) - \nabla \cdot \mathbf{j}_A + r_A \tag{3}$$

Sum Eq. 3 over species. The mass-frame definition gives $\sum_A \mathbf{j}_A = 0$, while ordinary chemical reaction conserves mass, $\sum_A r_A = 0$. With $\rho = \sum_A \rho_A$,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{4}$$

For constant mixture density,

$$\rho = \text{constant} \quad \Rightarrow \quad \nabla \cdot \mathbf{v} = 0$$

Constant mixture density does not require constant species density. A dilute solute may vary substantially while the solvent determines nearly all of ρ. The same overall continuity equation also applies in momentum transport.

4.2 Molar units and reference frame

Write $c_A = \rho_A / M_A$, with molar mass M_A in kg kmol⁻¹ and concentration c_A in kmol m⁻³. The molar production rate $R_A = r_A / M_A$ is in $\mathrm{kmol\,m^{-3}\,s^{-1}}$. Total molar flux $\mathbf{N}_A$ is in $\mathrm{kmol\,m^{-2}\,s^{-1}}$. Its exact decomposition uses the molar-average velocity $\mathbf{v}^*$ and its matching relative flux $\mathbf{J}_A$:

$$\begin{aligned}\mathbf{N}_A &= c_A\mathbf{v}^* + \mathbf{J}_A \\ \frac{\partial c_A}{\partial t} &= -\nabla\cdot(c_A\mathbf{v}^*) - \nabla\cdot\mathbf{J}_A + R_A \\ \frac{\partial c}{\partial t} &= -\nabla\cdot(c\mathbf{v}^*) + \sum_A R_A\end{aligned} \tag{5}$$

Here $c = \sum_A c_A$ and $\sum_A \mathbf{J}_A = 0$. Reaction conserves mass but may change molecule count. For example, $\mathrm{N_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{NH_3}$ consumes four moles and produces two. Equal total stoichiometric coefficients conserve moles; an isomerisation $\mathrm{A} \rightarrow \mathrm{B}$ is one example, rather than the only possibility.

4.3 Dilute liquids and low-density gases

For a binary dilute liquid at fixed temperature and pressure, approximate ρ and D_{AB} as constants. Diffusivity D_{AB} has units $\mathrm{m^2\,s^{-1}}$. Mass fraction $\omega_A = \rho_A/\rho$ is dimensionless. Fick's law then becomes

$$\mathbf{j}_A = -\rho D_{AB}\nabla\omega_A = -D_{AB}\nabla\rho_A \tag{6}$$

Use Eq. 4 to expand the convective divergence in Eq. 3. Divide by constant M_A to obtain

$$\begin{aligned}\frac{\partial \rho_A}{\partial t} + \mathbf{v}\cdot\nabla\rho_A &= D_{AB}\nabla^2\rho_A + r_A \\ \frac{\partial c_A}{\partial t} + \mathbf{v}\cdot\nabla c_A &= D_{AB}\nabla^2 c_A + R_A\end{aligned} \tag{7}$$

The dilute-liquid reduction still retains any imposed solvent velocity.

For an ideal low-density gas at fixed T and P, $c = P/(\mathcal{R}T)$ is constant. Gas mole fraction is $y_A = c_A/c$, following topic 1; the source uses x_A for gas and liquid alike. The binary law is

$$\mathbf{J}_A = -cD_{AB}\nabla y_A = -D_{AB}\nabla c_A.$$

Expanding Eq. 5 and summing it gives

$$\begin{aligned}\nabla\cdot\mathbf{v}^* &= \frac{\sum_A R_A}{c} \\ \frac{\partial c_A}{\partial t} + \mathbf{v}^*\cdot\nabla c_A &= D_{AB}\nabla^2 c_A + R_A - y_A\sum_A R_A\end{aligned} \tag{8}$$

The simpler gas convection-diffusion equation applies when $\sum_A R_A = 0$, including a nonreacting bulk gas. For a mole-changing homogeneous reaction, retain the additional term or justify its neglect by a suitable dilute approximation. All gas films below have no homogeneous reaction; their surface reaction sets a boundary condition. This distinction avoids assuming gas volume conservation during a mole-changing reaction. Pressure P is in Pa, T in K and $\mathcal{R} = 8314\ \mathrm{Pa\,m^3\,kmol^{-1}\,K^{-1}}$ when c is in $\mathrm{kmol\ m^{-3}}$.

With no flow and no reaction, the constant-property equation reduces to Fick's second law,

$$\frac{\partial c_A}{\partial t} = D_{AB}\nabla^2 c_A \tag{9}$$

QUIZ

1. Reaction and total moles

An ordinary chemical reaction conserves total mass. Must it also conserve the total number of moles?

1. Yes, for every reaction.
2. Yes, whenever temperature is constant.
3. No, because chemical reaction can destroy total mass.
4. No. A reaction can change the total number of moles while conserving mass.

See solution for Quiz 1

4.4 Curved coordinates

The divergence changes with geometry, while the conservation statement does not. With cylindrical coordinates r, θ, z, radial distance r in m and angle θ in radians,

$$\frac{\partial c_A}{\partial t} = -\frac{1}{r}\frac{\partial (r N_{Ar})}{\partial r} - \frac{1}{r}\frac{\partial N_{A\theta}}{\partial \theta} - \frac{\partial N_{Az}}{\partial z} + R_A \tag{10}$$

With spherical coordinates r, θ, ϕ, where θ is the polar angle and ϕ the azimuth,

$$\frac{\partial c_A}{\partial t} = -\frac{1}{r^2}\frac{\partial (r^2 N_{Ar})}{\partial r} - \frac{1}{r \sin\theta}\frac{\partial (N_{A\theta} \sin\theta)}{\partial \theta} - \frac{1}{r \sin\theta}\frac{\partial N_{A\phi}}{\partial \phi} + R_A \tag{11}$$

Cylindrical radial area grows as r; spherical radial area grows as r^2. Thus a steady radial problem with no volumetric reaction conserves rN_{Ar} in a cylinder and $r^2 N_{Ar}$ in a sphere. The local flux need not be constant even though the total rate is.

QUIZ

2. Radial flux in a cylindrical wall

A cylindrical wall carries a steady outward species rate with no reaction or end effects. What happens to the local radial flux when radius doubles within the wall?

1. It doubles.
2. It halves.
3. It stays the same.
4. It falls to one quarter.

See solution for Quiz 2

5 Case 1: diffusion of A through non-diffusing B

In a steady plane gas film with variation only in z, no accumulation, transverse gradients or bulk reaction remain in Eq. 5. Therefore $dN_{Az}/dz = 0$. Binary total flux combines diffusion and molar drift,

$$N_{Az} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{Az} + N_{Bz})$$

With $N_{Bz} = 0$, rearranging gives

$$N_{Az} = -\frac{cD_{AB}}{1 - y_A}\frac{dy_A}{dz} \tag{12}$$

Integrate the constant flux between z_1 and z_2, where $y_A = y_{A1}$ and y_{A2}. Separating $dy_A/(1 - y_A)$ gives

$$N_{Az} = \frac{cD_{AB}}{z_2 - z_1}\ln\frac{1 - y_{A2}}{1 - y_{A1}} \tag{13}$$

This reproduces the shell-balance result in topic 1 by deleting terms from the general equation. A heterogeneous reaction still leaves $R_A = 0$ in the film. The source uses the same method to extend the geometry.

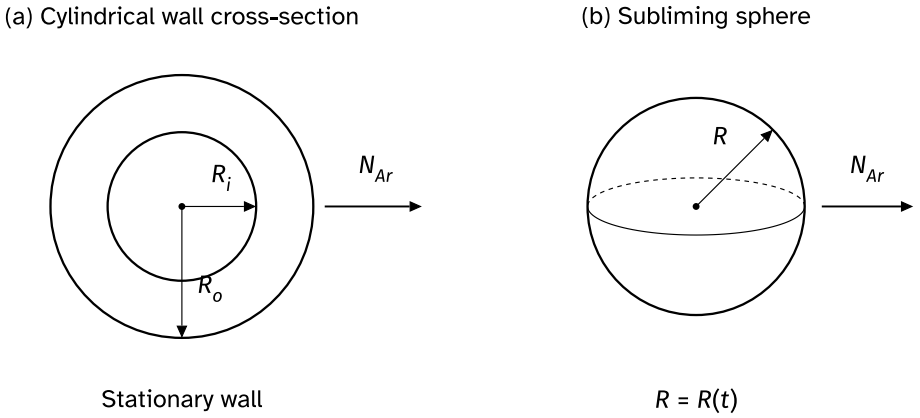


Figure 2: Radial diffusion through a stationary cylindrical wall and from a subliming sphere into still air.

EXERCISE

Exercise 1. Cylindrical wall

A given gas A can diffuse through the solid wall of a tube in which it flows. Find the rate of gas diffusion in terms of the tube dimensions (inside wall radius R_i, outside wall radius R_o), the gas-solid diffusivity, and the gas concentrations at the walls.

Assumptions:

- steady state
- flux in r direction only
- no chemical reaction
- A concentration in gas is quite dilute $\rightarrow x_A \sim 0$
- Constant D_{AB}

See solution for Exercise 1

EXERCISE
Exercise 2. Naphthalene sphere

A spherical ball of solid, nonporous naphthalene is suspended in still air. The naphthalene ball slowly sublimes, releasing naphthalene into the surrounding air. It may be assumed that the sublimation occurs as a molecular diffusion-limited process. Through consideration of the diffusion equation, estimate the time required to reduce the diameter of the ball from 2 to 0.5 cm when the surrounding air is at 347 K and 1 atm.

Data for naphthalene:

- MW = 128 g/mol
- Density = 1.145 g/cm^3
- Diffusivity in air = $8.19 \times 10^{-6}\ \mathrm{m}^2/\mathrm{s}$
- Vapour pressure = 666 Pa at 347 K

See solution for Exercise 2

6 Case 2: diffusion with a surface reaction

6.1 A surface reaction and flux stoichiometry

DEFINITION
Heterogeneous reaction

A reaction at an interface between phases, such as a gas reacting at a catalyst surface. It supplies a species-flux boundary condition.

A gas film of thickness δ surrounds a catalyst. Coordinate z increases from the bulk-film edge at $z = 0$ toward the surface at $z = \delta$. Bulk A has fraction y_{A0}. At the surface, the irreversible instantaneous reaction $2\mathrm{A} \rightarrow \mathrm{B}$ consumes two moles of A for each mole of B returning through the film. There is no homogeneous reaction in the gas. Constant T, P and D_{AB} make c and diffusivity constant; this case need not be dilute.

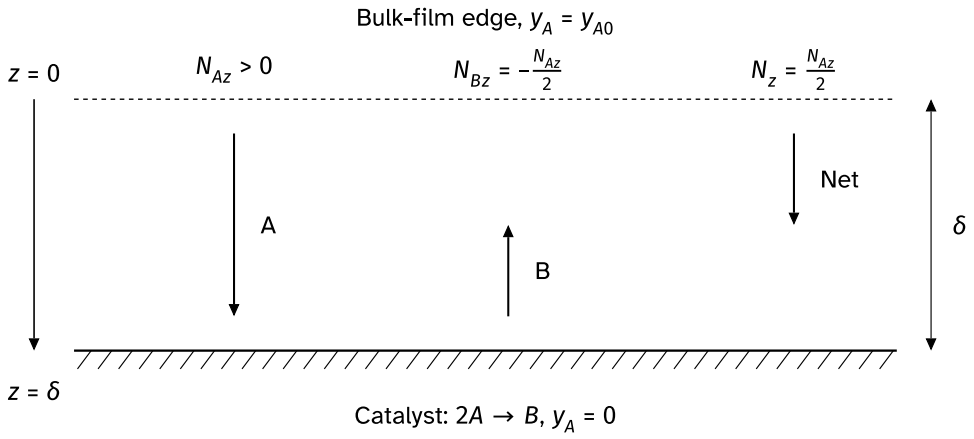


Figure 4: Molar fluxes through a nonreacting gas film toward a catalyst where two moles of A form one mole of B. Positive z points toward the catalyst. The outward B flux has half the magnitude of the inward A flux, leaving a net molar flux toward the surface.

The stoichiometric boundary fixes $N_{Bz} = -N_{Az}/2$. Steady nonreacting gas conserves both fluxes throughout the film. Substitute the ratio into the total-flux law,

$$\begin{aligned} N_{Az} &= -cD_{AB}\frac{dy_A}{dz} + \frac{1}{2}y_A N_{Az} \\ N_{Az} &= -\frac{cD_{AB}}{1-\frac{y_A}{2}}\frac{dy_A}{dz} \end{aligned} \tag{19}$$

The net flux $N_{Az} + N_{Bz} = N_{Az}/2$ points toward the catalyst. Molar drift carries A along with diffusion. More generally $N_B = -\beta N_A$ gives denominator $1 - (1-\beta)y_A$. Equimolar counter-diffusion has $\beta = 1$, stagnant B has $\beta = 0$, and this reaction has $\beta = 1/2$.

QUIZ

3. Surface-reaction stoichiometry

At a catalyst, $2A \rightarrow B$. Positive flux points toward the catalyst. If $N_A > 0$, which flux relation holds in the steady nonreacting gas film?

1. $N_B = -N_A/2$.
2. $N_B = -N_A$.
3. $N_B = 0$.
4. $N_B = 2N_A$.

See solution for Quiz 3

6.2 Integration and instantaneous boundary

Since $dN_{Az}/dz = 0$, substitute Eq. 19 and remove constant cD_{AB}. Integrate twice,

$$\begin{aligned}\frac{d}{dz}\left(\frac{1}{1-\frac{y_A}{2}}\frac{dy_A}{dz}\right)&=0\\ \frac{1}{1-\frac{y_A}{2}}\frac{dy_A}{dz}&=C_1\\ -2\ln\left(1-\frac{y_A}{2}\right)&=C_1 z+C_2\end{aligned}\tag{20}$$

Here C_1 is in m⁻¹ and C_2 dimensionless. The factor two comes from the derivative of $1-y_A/2$. The source rewrites this as

$$1-\frac{y_A}{2}=K_1^z K_2.$$

We use a dimensionless coordinate ratio instead of a dimensional exponent. Instantaneous reaction leaves $y_A(\delta)=0$, while bulk supply sets $y_A(0)=y_{A0}$. Thus

$$C_2=-2\ln\left(1-\frac{y_{A0}}{2}\right)$$

and $C_1=-C_2/\delta$. Substitution gives

$$\begin{aligned}1-\frac{y_A(z)}{2}&=\left(1-\frac{y_{A0}}{2}\right)^{1-\frac{z}{\delta}}\\ N_{Az}&=\frac{2cD_{AB}}{\delta}\ln\frac{1}{1-\frac{y_{A0}}{2}}\end{aligned}\tag{21}$$

Both endpoints hold. The flux is positive toward the catalyst. At small y_{A0} the logarithm is approximately $y_{A0}/2$, so

$$N_{Az}\approx\frac{cD_{AB}y_{A0}}{\delta},$$

the dilute Fick result. At bulk fractions 0.2 and 0.8 the exact rate exceeds that approximation by about 5.36 and 27.7 percent respectively. Complementary $y_B=1-y_A$ ensures binary fractions sum to one. The film is a model of a continuous boundary layer; δ is an equivalent thickness determined by flow, rather than a sharp physical boundary. Thinning it increases rate per area. Increasing total catalyst area can also increase total rate, even when a faster intrinsic rate per area cannot.

6.3 Finite surface kinetics

If reaction is finite, the A-consumption law is

$$N_{Az}=k_1''c_{As}=k_1''cy_{As}$$

at the surface. Surface coefficient k_1'' is in m s⁻¹ and c_{As} is the unknown dissolved or gas surface concentration appropriate to this model. The exact film equation is

$$N_{Az} = \frac{2cD_{AB}}{\delta} \ln \frac{1 - \frac{y_{As}}{2}}{1 - \frac{y_{A0}}{2}}$$
$$y_{As} = \frac{N_{Az}}{k_1'' c} \tag{22}$$

Solve these together; a finite surface concentration is allowed. In the dilute limit define $k_c = D_{AB}/\delta$ in m s⁻¹. Equating $k_c(c_{A0} - c_{As})$ to $k_1'' c_{As}$ yields

$$c_{As} = \frac{k_c c_{A0}}{k_c + k_1''}$$
$$N_A = \frac{c_{A0}}{\frac{1}{k_c} + \frac{1}{k_1''}} \tag{23}$$

DEFINITION
Damköhler number

A dimensionless ratio of reaction rate to transport rate. For this first-order surface reaction and gas film,

$$\mathrm{Da} = \frac{k_1''}{k_c} = \frac{k_1'' \delta}{D_{AB}}.$$

Large Da means diffusion controls; small Da means surface reaction controls.

For this film,

$$\mathrm{Da} = \frac{k_1'' \delta}{D_{AB}}$$

Both resistances have units s m⁻¹. Their relative sizes identify the useful limiting model:

- For $\mathrm{Da} < 0.1$, surface reaction resistance exceeds film resistance by more than tenfold. The surface concentration is close to the bulk concentration, and faster kinetics increases the rate.
- For $0.1 \leq \mathrm{Da} \leq 10$, both resistances can affect the rate. Retain the film balance and the surface reaction law.
- For $\mathrm{Da} > 10$, film resistance exceeds surface reaction resistance by more than tenfold. A nearly zero surface concentration is a useful limiting approximation, and improving film transport increases the rate.

The cutoffs mark resistance ratios, rather than sharp changes in behaviour. Neglecting the smaller resistance at a ratio of ten overpredicts the overall rate by ten percent in this linear model.

For $k_1'' = 10^{-3}$ and $k_c = 10^{-5}\ \mathrm{m\,s^{-1}}$, $\mathrm{Da} = 100$ and $c_{As}/c_{A0} = 1/101$. Increasing transport is more effective than increasing an already fast surface reaction. If the ratio is 0.01 instead, the surface concentration is about 99 percent of the bulk value and kinetics controls. This definition is for a first-order surface coefficient in m s⁻¹; inserting the homogeneous coefficient in $\mathrm{s^{-1}}$ would leave a dimensional quantity. The homogeneous comparison below uses a volumetric reaction coefficient and its own diffusion scale.

QUIZ

4. Surface kinetics versus film transport

A dilute film model has surface Damköhler number $\mathrm{Da} = k_1''/k_c = 100$. Which change most directly increases the rate when the bulk concentration is held fixed?

1. Increase an already very fast surface reaction coefficient alone.
2. Make the diffusion film thicker.
3. Increase the film mass transfer coefficient.
4. Reduce the bulk concentration.

See solution for Quiz 4

7 Case 3: diffusion with a zero-order homogeneous reaction

7.1 Zero-order consumption

DEFINITION

Homogeneous reaction

A reaction occurring within a phase volume. Its production or consumption rate appears as a volumetric source in the species balance.

Gas A dissolves into liquid B at an interface and diffuses down a pool of depth L. Reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$ consumes A throughout the liquid. Treat A and product AB as dilute, the solvent as stationary, and T and D_{AB} as constant. Let x measure depth from the interface. The bottom is impermeable. Zero-order consumption has $R_A = -k_0$, with positive k_0 in kmol m^{-3} s^{-1}, independent of concentration within the range where the kinetics remain valid.

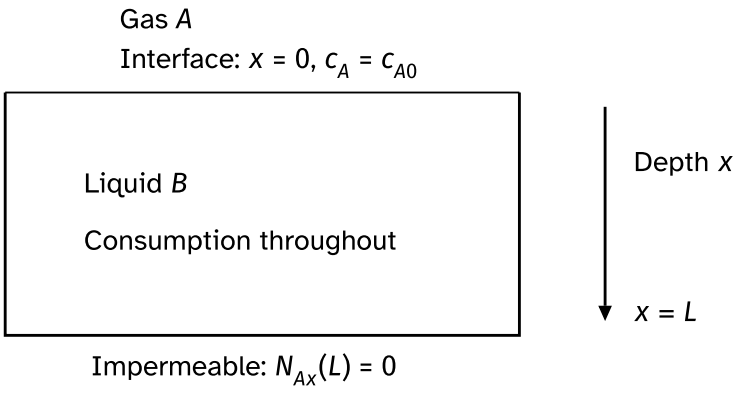


Figure 5: A dissolves at the upper surface of a stationary liquid layer and reacts throughout its depth. The bottom is impermeable.

Steady, one-dimensional continuity is

$$-\frac{dN_{Ax}}{dx} + R_A = 0.$$

Dilution and absence of solvent flow give

$$N_{Ax} = -D_{AB}\frac{dc_A}{dx}.$$

Substituting $R_A = -k_0$ therefore gives

$$D_{AB}\frac{d^2c_A}{dx^2} - k_0 = 0 \tag{24}$$

Both terms are kmol m⁻³ s⁻¹. Integrate twice,

$$\begin{aligned} \frac{dc_A}{dx} &= \frac{k_0}{D_{AB}}x + a \\ c_A &= \frac{k_0}{2D_{AB}}x^2 + ax + b \end{aligned} \tag{25}$$

The interface sets $c_A(0) = c_{A0}$ by gas-liquid equilibrium, for example a measured Henry solubility at the given temperature. An impermeable bottom sets $N_{Ax}(L) = 0$, equivalent here to

$$\left[\frac{dc_A}{dx}\right]_{x=L} = 0.$$

Thus $a = -k_0L/D_{AB}$ in kmol m⁻⁴ and $b = c_{A0}$ in kmol m⁻³. Use x for depth in both boundary conditions. The result and flux are

$$\begin{aligned} c_A &= c_{A0} + \frac{k_0}{2D_{AB}}(x^2 - 2Lx) \\ N_{Ax}(x) &= k_0(L - x) \\ N_{Ax}(0) &= k_0L \end{aligned} \tag{26}$$

Concentration decreases with depth and its gradient vanishes at the bottom. Surface influx equals the integrated consumption k_0L, independently checking the balance. The bottom concentration is

$$c_{A0} - \frac{k_0L^2}{2D_{AB}}.$$

This full-depth solution requires

$$\frac{k_0L^2}{2D_{AB}c_{A0}} \leq 1.$$

Equality puts zero concentration exactly at the bottom. Beyond it, negative concentrations are unphysical. A consumes completely at

$$x^* = \sqrt{\frac{2D_{AB}c_{A0}}{k_0}} < L;$$

impose both $c_A = 0$ and zero flux there and stop consumption below that depth. A zero-order law cannot continue consuming an absent reactant.

QUIZ

5. An unphysical zero-order profile

The full-depth zero-order consumption solution predicts a negative concentration near the impermeable bottom. How should this result be interpreted?

1. The full-depth solution remains valid because the overall balance closes.
2. The reactant has run out in part of the liquid, so the model must stop consumption there.
3. A first-order rate law can be substituted without changing the solution.
4. The impermeable-bottom condition requires a negative bottom concentration.

See solution for Quiz 5

8 Case 4: diffusion with a first-order homogeneous reaction

8.1 First-order consumption and equation

Keep the same stationary dilute liquid, interface concentration and impermeable bottom, but use $R_A = -k_1''' c_A$. Volumetric coefficient k_1''' is in s⁻¹, distinct from surface k_1'' in m s⁻¹. Reaction now slows as A disappears. Substitute the rate and Fick's law into the same steady balance,

$$D_{AB}\frac{d^2 c_A}{dx^2} - k_1''' c_A = 0 \tag{27}$$

Define

$$m = \sqrt{\frac{k_1'''}{D_{AB}}}$$

Both terms have concentration-per-time units. Parameter m is in m⁻¹, so $1/m$ is the penetration length. It follows by equating diffusion time ℓ^2/D_{AB} to reaction time $1/k_1'''$. This is the fin equation with excess temperature replaced by concentration.

8.2 Solution, surface flux and limits

DEFINITION

Effectiveness factor

The actual overall reaction rate divided by the rate if the reacting region were everywhere at the reference surface concentration under the same kinetic and temperature assumptions. It measures the effect of internal concentration gradients.

DEFINITION
Fin efficiency

The heat transferred by a fin divided by the heat it would transfer if its entire surface were at the base temperature, with the same surface coefficient and surroundings. For a uniform straight fin with insulated tip,

$$\eta_f = \frac{\tanh(m_f L)}{m_f L},$$

where

$$m_f = \sqrt{\frac{hP}{k_s A_c}},$$

P is exposed perimeter and A_c is the conduction cross-section. It is analogous to reaction effectiveness.

Both ratios approach one for small internal gradients and fall below one as those gradients grow. The fin parameter m_f uses solid conductivity; the reaction parameter m uses species diffusivity and kinetics. Their similar equations do not make those parameters interchangeable.

DEFINITION
Hatta number

A dimensionless measure of reaction relative to diffusion for a homogeneous reaction. These notes use the pool-depth convention

$$\mathrm{Ha} = mL = L\sqrt{\frac{k_1'''}{D_{AB}}},$$

the pool depth divided by the reaction penetration length. In absorption film models the length is an equivalent film thickness instead of pool depth. Here k_1''' is a first-order volumetric coefficient in s^{-1}.

For this first-order pool model, Hatta number indicates how much of the liquid depth participates in reaction:

- For $\mathrm{Ha} < 0.3$, diffusion can replenish A throughout the depth faster than reaction consumes it. Concentration is nearly uniform, reaction controls, and uptake is approximately proportional to depth.
- For $0.3 \leq \mathrm{Ha} \leq 3$, concentration gradients and reaction both affect uptake. Use the full reaction and diffusion solution below.
- For $\mathrm{Ha} > 3$, A is consumed within a thin region near the interface. Additional depth has little effect on uptake; both diffusivity and reaction kinetics determine the rate in that region.

These approximate limits apply to the stated depth convention and boundary conditions. The flux limits below differ from the exact result by about three percent at $\mathrm{Ha} = 0.3$ and half a percent at $\mathrm{Ha} = 3$.

The general solution is

$$c_A = C_1 e^{mx} + C_2 e^{-mx}.$$

Both constants have concentration units. At $x = L$, zero gradient requires $C_2 = C_1 e^{2mL}$. At $x = 0$, $C_1 + C_2 = c_{A0}$. Thus

$$C_1 = \frac{c_{A0}}{1 + e^{2mL}}$$

and

$$C_2 = \frac{c_{A0} e^{2mL}}{1 + e^{2mL}}.$$

Equivalently,

$$\begin{aligned} c_A &= c_{A0}[\cosh(mx) - \tanh(mL)\sinh(mx)] \\ \frac{c_A}{c_{A0}} &= \frac{\cosh[m(L-x)]}{\cosh(mL)} \\ c_A(L) &= \frac{c_{A0}}{\cosh(mL)} \end{aligned} \tag{28}$$

The difference-of-arguments identity converts the source's expression to the ratio. Both boundaries hold and concentration stays positive for finite positive data. Differentiate Eq. 28 and multiply by $-D_{AB}$,

$$\begin{aligned} N_{Ax}(x) &= c_{A0} D_{AB} m \frac{\sinh[m(L-x)]}{\cosh(mL)} \\ N_{Ax}(0) &= +c_{A0} D_{AB} m \tanh(mL) \end{aligned} \tag{29}$$

The gradient is negative at the surface, so influx must be positive in $+x$. Integrating $k_1''' c_A$ over $0 \le x \le L$ reproduces the positive surface flux.

For $\mathrm{Ha} \ll 1$, $\tanh \mathrm{Ha} \approx \mathrm{Ha}$, giving

$$N_{Ax}(0) \approx c_{A0} k_1''' L.$$

For $\mathrm{Ha} \gg 1$, $\tanh \mathrm{Ha} \approx 1$, giving

$$N_{Ax}(0) \approx c_{A0} \sqrt{k_1''' D_{AB}}.$$

The effectiveness factor is

$$\eta = \frac{\tanh(\mathrm{Ha})}{\mathrm{Ha}},$$

the same function as the insulated-tip fin efficiency.

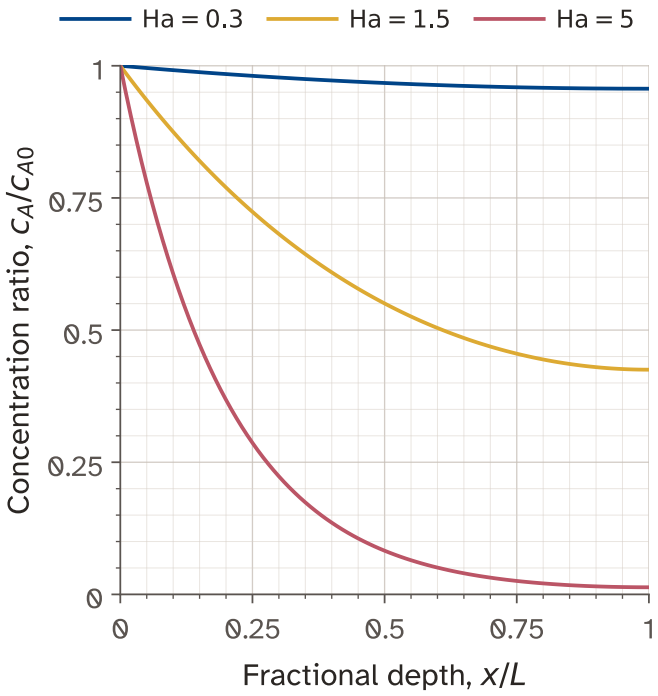


Figure 6: First-order concentration profiles at Hatta numbers 0.3, 1.5 and 5. Larger Hatta numbers confine consumption closer to the interface.

The curves follow Eq. 28.

For $L = 10^{-3}$ m, $k_1''' = 1\ \mathrm{s}^{-1}$ and $D_{AB} = 10^{-9}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, $\mathrm{Ha} = 31.6$. The reaction penetrates only about $32\ \mu\mathrm{m}$, so adding depth has little effect on uptake. Reducing L to 10^{-5} m gives $\mathrm{Ha} = 0.316$, close to the uniform-concentration limit. Check whether a quoted length is pool depth or film thickness before applying either limit.

QUIZ

6. First-order penetration depth

In the stated first-order pool model,

$$\mathrm{Ha} = L\sqrt{\frac{k_1'''}{D_{AB}}} \gg 1.$$

With fixed surface concentration, what does adding more pool depth do to surface uptake?

1. It increases uptake in direct proportion to depth indefinitely.
2. It makes concentration uniform throughout the pool.
3. It reverses the surface flux.
4. It changes uptake very little because A is consumed close to the surface.

See solution for Quiz 6

9 Classroom example: catalytic tube

9.1 Species advection versus diffusion

Use Péclet number with species diffusivity to decide whether axial diffusion can be neglected. With mean speed $\bar{v}$ and axial length L, $\mathrm{Pe}_{m,L} = \bar{v}L/D_{AB}$; small values require axial diffusion, while large values support omitting it away from end regions. The example below gives 10^7 for $\bar{v} = 0.1\ \mathrm{m\,s^{-1}}$, $L = 0.1\ \mathrm{m}$ and $D_{AB} = 10^{-9}\ \mathrm{m^2\,s^{-1}}$. This compares axial terms, so radial diffusion still supplies the wall. Using tube radius as the axial scale or evaluating this bulk estimate at a zero-velocity wall would answer a different question. The thermal version uses α instead of D_{AB}.

EXERCISE
Exercise 3. Catalytic tube

Consider a catalytic tubular reactor, where a dilute solution of solute A in solvent S is in fully developed, laminar flow in the region $z < 0$. It encounters the catalytic wall in the region $0 \leq z \leq L$, where solute A is instantaneously and irreversibly rearranged to an isomer B. Write the appropriate diffusion equation (in differential form) for this problem, along with the boundary conditions. Assume that the flow is isothermal and neglect the presence of B.

See solution for Exercise 3

10 Additional examples

EXERCISE
Exercise 4. Derive a film balance with finite surface reaction

A dilute gas species A crosses a plane film to a catalyst, where it undergoes an isomerisation $A \to B$. The gas is at 500 K and 100 kPa. The bulk mole fraction is 0.020, film thickness is 1.5 mm, diffusivity is 6.0×10^{-5} m² s⁻¹ and surface rate constant is $k_s = 0.015$ m s⁻¹. The catalyst area is 0.040 m². Assume steady one-dimensional isothermal transport with constant pressure and diffusivity, no gas-phase reaction, and negligible normal bulk velocity. Let $z = 0$ be the bulk edge and $z = L$ the catalyst.

Derive the concentration profile from a shell balance. Find the surface mole fraction and molar removal rate. Which resistance is greater, and what happens in the limits of very slow and very fast surface reaction?

See solution for Exercise 4

EXERCISE
Exercise 5. Use reaction stoichiometry to determine flux directions

At a catalyst, gas R reacts by $R \to 2P$. Take the coordinate direction towards the catalyst and suppose $N_R = 0.010$ mol m⁻² s⁻¹. Find N_P and the total molar flux. Is equimolar

counter-diffusion appropriate? Compare with a reaction $R \to P$ at the same reactant flux.

See solution for Exercise 5

EXERCISE

Exercise 6. Distinguish reaction throughout a liquid from reaction at a wall

An idealised stationary water layer of depth 0.010 m absorbs oxygen at its upper face. That face is held at $c_{A0} = 0.25$ mol m⁻³. Oxygen consumption throughout the liquid follows $R_A = -k_1''' c_A$, with $k_1''' = 0.0020$ s⁻¹ and $D_{AB} = 2.0 \times 10^{-9}$ m² s⁻¹. The bottom is impermeable. Assume a steady one-dimensional profile and constant properties.

Formulate the problem and estimate the oxygen influx. Explain how the model would change if consumption occurred only on a catalytic bottom instead.

See solution for Exercise 6

EXERCISE

Exercise 7. An expanding reaction mixture changes the film profile

A catalyst converts gas A instantaneously by $A \to 3B$. A plane gas film of thickness $\delta = 2.0$ mm separates the surface from a well-mixed bulk gas with $y_{A0} = 0.20$. The binary gas is at 500 K and 1.5 bar, with $D_{AB} = 2.0 \times 10^{-5}$ m² s⁻¹. Assume steady, one-dimensional transport, constant temperature, pressure and diffusivity, and no reaction inside the film. The catalyst is impermeable except for the reactant and product exchange specified by the reaction.

Taking z from the bulk edge towards the catalyst, derive $y_A(z)$ and the inward flux of A. Compare with equimolar counter-diffusion across the same film. Does a constant species flux imply a linear mole-fraction profile?

See solution for Exercise 7

11 What you should now be able to calculate

Distinguish surface and volume reaction, combine finite reaction and diffusion resistance, and use stoichiometry to determine total molar motion.

Practice: Workshop 9 for surface reaction and coupled species fluxes.

12 Report an error

Email Ranjeet Utikar with the title Species balances and diffusion with reaction, the URL `/mass-transport/diffusion-with-reaction/`, and the equation or passage to check.

References

Bird, R. Byron, Warren E. Stewart, and Edwin N. Lightfoot. 2006. *Transport Phenomena*. Revised 2nd. John Wiley & Sons. https://www.wiley-vch.de/en/areas-interest/engineering/transport-phenomena-978-0-470-11539-8.

Geankoplis, Christie J. 2003. *Transport Processes and Separation Process Principles*. 4th ed. Prentice Hall.

Shah, Milinkumar. n.d. "CHEN3001-TP: Mass Transport 2." Curtin University. Unpublished.

Welty, James R., Charles E. Wicks, Robert E. Wilson, and Gregory L. Rorrer. 2001. *Fundamentals of Momentum, Heat, and Mass Transfer*. 4th ed. John Wiley & Sons.

Solutions

Quiz solutions

Quiz 1. Reaction and total moles

Correct choice: 4.

A reaction conserves mass, but can change the total number of moles. For example, one mole of nitrogen and three moles of hydrogen form two moles of ammonia. The mass is unchanged even though four moles become two.

Back to Quiz 1

Quiz 2. Radial flux in a cylindrical wall

Correct choice: 2.

The same molar rate crosses each cylindrical surface:

$$\dot{n}_A = 2\pi r L N_{Ar}$$

Doubling radius doubles the area. Therefore,

$$\frac{N_{Ar}(2r)}{N_{Ar}(r)} = \frac{1}{2}$$

The local flux halves.

Back to Quiz 2

Quiz 3. Surface-reaction stoichiometry

Correct choice: 1.

For every two moles of A consumed, one mole of B leaves the catalyst. Since positive flux points toward the catalyst,

$$N_B = -\frac{N_A}{2}$$

The negative sign means that B moves away from the catalyst. The net molar flux is

$$N_A + N_B = \frac{N_A}{2}$$

It points toward the catalyst.

Back to Quiz 3

Quiz 4. Surface kinetics versus film transport

Correct choice: 3.

The ratio of the surface reaction coefficient to the film coefficient is

$$\mathrm{Da} = \frac{k_1''}{k_c} = 100$$

Reaction is much faster than transport through the film. The uptake is approximately

$$N_A \simeq k_c c_{A0}$$

Increasing the film coefficient increases the rate. Making an already fast surface reaction faster has little effect.

Back to Quiz 4

Quiz 5. An unphysical zero-order profile

Correct choice: 2.

Zero-order consumption cannot continue where reactant is absent. The full-depth solution requires a nonnegative concentration throughout. Beyond its validity limit, locate a depletion depth with zero concentration and zero flux and stop consumption below it.

Back to Quiz 5

Quiz 6. First-order penetration depth

Correct choice: 4.

The distance over which A penetrates before reacting is approximately

$$\ell = \sqrt{\frac{D_{AB}}{k_1'''}}$$

At large Hatta number this distance is much smaller than the pool depth. The surface flux approaches

$$N_{A0} \simeq c_{A0}\sqrt{k_1''' D_{AB}}$$

Adding liquid below the thin reacting region changes the uptake very little.

Back to Quiz 6

Exercise solutions

Exercise 1. Cylindrical wall

The radial shell in Figure 3 shows why a cylindrical balance must account for the changing area.

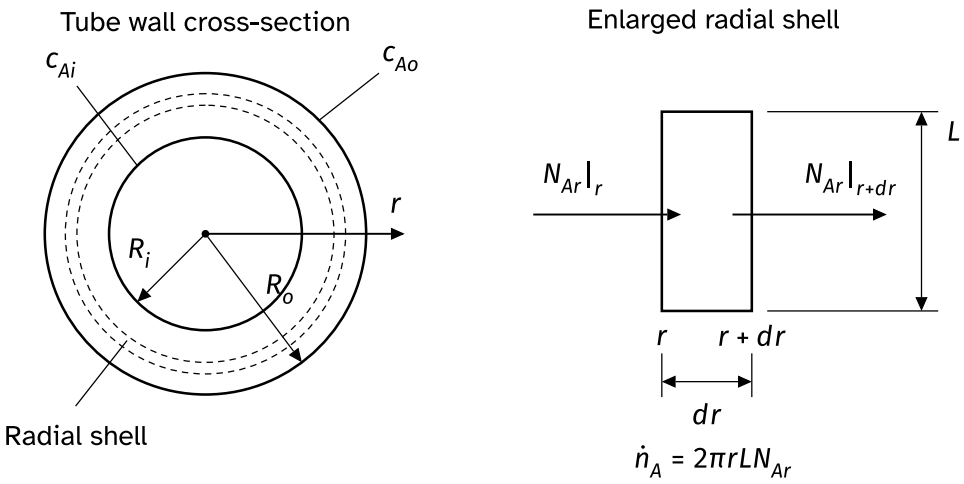


Figure 3: A stationary cylindrical wall and an enlarged radial shell. The molar rate equals the local flux multiplied by the cylindrical area 2πrL.

Data

Quantity	Value
Inner wall radius	R_i
Outer wall radius	R_o
Axial length	L
Constant gas-solid diffusivity	D_{AB}
Dissolved concentration at the inner face	c_{Ai} in $\mathrm{kmol\,m^{-3}}$
Dissolved concentration at the outer face	c_{Ao} in $\mathrm{kmol\,m^{-3}}$

Assumptions

- Steady state.
- Radial diffusion only.
- No chemical reaction.
- Dilute dissolved A in a stationary solid matrix.
- Constant diffusivity.
- Negligible end effects.

Calculations

Choose positive flux radially outwards. A steady shell has no accumulation or reaction, so its inward and outward molar rates are equal. From Eq. 10, the governing radial balance is

$$\frac{d}{dr}(rN_{Ar}) = 0$$

Consequently, the total outward molar rate is independent of radius,

$$\dot{n}_A = 2\pi r L N_{Ar}$$

The source denotes this rate by W_A. In a stationary solid, transport of dilute dissolved A follows Fick's law,

$$N_{Ar} = -D_{AB}\frac{dc_A}{dr}$$

Substitute the flux into the rate expression, separate the variables and integrate between the two wall faces,

$$\dot{n}_A \int_{R_i}^{R_o} \frac{dr}{r} = -2\pi L D_{AB} \int_{c_{Ai}}^{c_{Ao}} dc_A$$

$$\dot{n}_A \ln\frac{R_o}{R_i} = 2\pi L D_{AB}(c_{Ai} - c_{Ao})$$

Solving for the rate gives

$$\dot{n}_A = \frac{2\pi L D_{AB}(c_{Ai} - c_{Ao})}{\ln\left(\frac{R_o}{R_i}\right)} \tag{14}$$

The concentration profile follows from the same differential equation. Since $r\,dc_A/dr$ is constant, integration from R_i to an arbitrary radius r gives

$$c_A(r) - c_{Ai} = C_1 \ln\left(\frac{r}{R_i}\right)$$

At $r = R_o$, impose $c_A = c_{Ao}$ to obtain

$$C_1 = \frac{c_{Ao} - c_{Ai}}{\ln\left(\frac{R_o}{R_i}\right)}.$$

Therefore

$$\frac{c_A - c_{Ai}}{c_{Ao} - c_{Ai}} = \frac{\ln\left(\frac{r}{R_i}\right)}{\ln\left(\frac{R_o}{R_i}\right)} \tag{15}$$

The profile recovers both specified wall concentrations. When $c_{Ai} > c_{Ao}$, its gradient is negative and the rate is positive outwards. The units of Eq. 14 are

$$\mathrm{m}\,(\mathrm{m^2\,s^{-1}})(\mathrm{kmol\,m^{-3}}) = \mathrm{kmol\,s^{-1}}.$$

The concentration-based resistance is

$$\frac{\ln\left(\frac{R_o}{R_i}\right)}{2\pi L D_{AB}},$$

in $\mathrm{s\,m^{-3}}$. Define the log-mean area,

$$A_{\mathrm{lm}} = \frac{2\pi L(R_o - R_i)}{\ln\left(\frac{R_o}{R_i}\right)}$$

The rate can then be written as

$$\dot{n}_A = \frac{D_{AB} A_{\mathrm{lm}} (c_{Ai} - c_{Ao})}{R_o - R_i},$$

just as cylindrical conduction can be written using a log-mean area.

The specified concentrations must be concentrations dissolved in the solid. A bulk gas concentration requires a solubility relation before it can be used as a wall boundary condition. For example, $c_A = S_A p_A$, with S_A in $\mathrm{kmol\,m^{-3}\,Pa^{-1}}$, gives the permeability $D_{AB} S_A$.

Answer

The outward molar rate is

$$\dot{n}_A = \frac{2\pi L D_{AB} (c_{Ai} - c_{Ao})}{\ln\left(\frac{R_o}{R_i}\right)}.$$

It is positive when the dissolved concentration is greater at the inner wall. The logarithmic concentration profile is given by Eq. 15.

Back to Exercise 1

Exercise 2. Naphthalene sphere

The spherical geometry in Figure 2 applies at each instantaneous ball radius. Vapour diffuses outwards through air while the solid surface slowly recedes.

Data

Quantity	Value
Temperature	$T = 347\ \mathrm{K}$
Pressure	$P = 1\ \mathrm{atm} = 101325\ \mathrm{Pa}$
Diffusivity	$D_{AB} = 8.19 \times 10^{-6}\ \mathrm{m^2\,s^{-1}}$
Saturation pressure	$p_A^{\mathrm{sat}} = 666\ \mathrm{Pa}$
Solid density	$\rho_s = 1145\ \mathrm{kg\,m^{-3}}$
Molar mass	$M_A = 128\ \mathrm{kg\,kmol^{-1}}$
Initial radius	$R_i = 0.010\ \mathrm{m}$
Final radius	$R_f = 0.0025\ \mathrm{m}$

The supplied dimensions are diameters. The table gives the corresponding radii.

Assumptions

- Spherically symmetric diffusion.
- Pseudo-steady gas profile as the surface recedes.
- Isothermal sublimation at 347 K.
- Ideal gas behaviour.
- Constant pressure, diffusivity and solid density.
- Vapour-solid equilibrium at the surface.
- Negligible naphthalene concentration far from the ball.
- Zero net air flux through the solid surface.
- Negligible natural convection and gas-phase reaction.

Calculations

From Eq. 11 at a fixed instantaneous radius, the steady radial balance gives

$$\frac{d(r^2 N_{Ar})}{dr} = 0.$$

The same total rate crosses each concentric sphere,

$$\dot{n}_A = 4\pi r^2 N_{Ar}$$

Air cannot cross the solid surface, so $N_{Br} = 0$. Writing Eq. 12 in radial form retains the resulting molar flow,

$$N_{Ar} = -\frac{cD_{AB}}{1 - y_A}\frac{dy_A}{dr}$$

Substituting the rate and integrating between radii R_1 and R_2 gives

$$\frac{\dot{n}_A}{4\pi c D_{AB}} \int_{R_1}^{R_2} \frac{dr}{r^2} = -\int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1-y_A}$$

Evaluating both integrals and solving for the rate gives

$$\dot{n}_A = \frac{4\pi c D_{AB}}{\frac{1}{R_1} - \frac{1}{R_2}} \ln \frac{1-y_{A2}}{1-y_{A1}} \tag{16}$$

For an effectively infinite surrounding gas, take $R_1 = R$, $R_2 \to \infty$ and $y_{A2} = 0$. Surface equilibrium and the ideal gas relation give

$$y_{As} = \frac{p_A^{\mathrm{sat}}}{P} = \frac{666}{101325} = 0.00657291$$

$$c = \frac{P}{R_u T} = \frac{101325}{8314(347)} = 0.0351218 \ \mathrm{kmol\,m^{-3}}$$

Define the constant composition factor,

$$F = \ln \frac{1}{1-y_{As}} = 0.00659461$$

The instantaneous sublimation rate is then $\dot{n}_A = 4\pi R c D_{AB} F$. The sphere loses moles as its radius decreases. Differentiating its solid inventory gives

$$\dot{n}_A = -\frac{d}{dt}\left(\frac{\rho_s}{M_A}\frac{4\pi R^3}{3}\right) = -\frac{\rho_s}{M_A} 4\pi R^2 \frac{dR}{dt}$$

Equate surface loss to diffusion into the gas. After cancelling $4\pi R$ and separating variables,

$$\begin{aligned} R\,dR &= -\frac{M_A c D_{AB} F}{\rho_s}\,dt \\ \int_{R_i}^{R_f} R\,dR &= -\frac{M_A c D_{AB} F}{\rho_s} \int_0^t dt \\ t &= \frac{\rho_s (R_i^2 - R_f^2)}{2 M_A c D_{AB} F} \end{aligned} \tag{17}$$

Substitute the radii and properties on a consistent kmol basis,

$$t = \frac{1145(0.010^2 - 0.0025^2)}{2(128)(0.0351218)(8.19\times10^{-6})(0.00659461)} = 2.210\times10^5\ \mathrm{s} = 61.40\ \mathrm{h} \tag{18}$$

The gas adjustment time is

$$\frac{R_i^2}{D_{AB}} = \frac{0.010^2}{8.19\times10^{-6}} = 12.2\ \mathrm{s},$$

much shorter than the sublimation time. This supports a pseudo-steady gas profile. Replacing F by the dilute approximation y_{As} gives 61.60 h, only 0.33 percent higher.

The integrated balance can also be expressed as a diameter-square law,

$$d^2 = d_i^2 - Kt$$

$$K = \frac{8 M_A c D_{AB} F}{\rho_s}$$

Here K has units $\mathrm{m^2\,s^{-1}}$. The composition factor must remain in K because the vapour pressure determines the driving force. A different thermal model would be needed if sublimation cooling changes the surface temperature appreciably.

Answer

The diffusion-limited model predicts $t = 2.21 \times 10^5$ s, or about 61.4 h, for the diameter to decrease from 2 cm to 0.5 cm.

Back to Exercise 2

Exercise 3. Catalytic tube

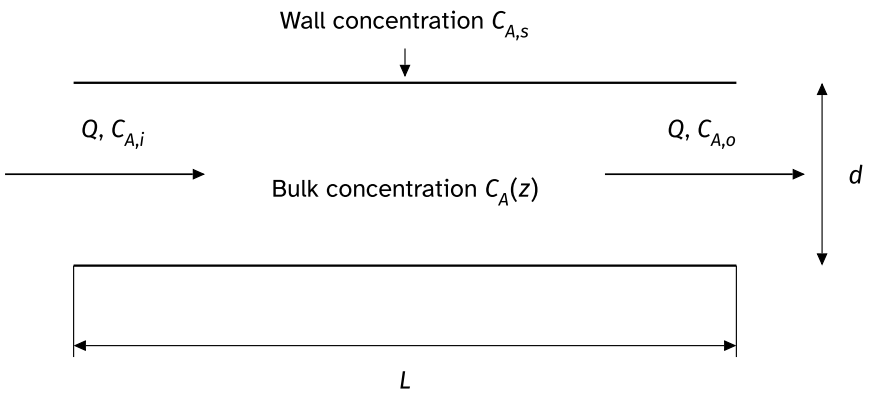


Figure 7: Axial liquid flow in a tube with a catalytic wall. For the instantaneous wall reaction, the labelled wall concentration is zero. Species A is consumed at the wall as the liquid flows downstream.

In this diagram, $d = 2R$ and $Q = \bar{v}\pi R^2$. Its concentration labels denote the molar concentration c_A used below.

Data

- Tube radius R
- Catalyst-coated length $0 \le z \le L$
- Mean axial velocity $\bar{v}$
- Uniform inlet concentration c_{A0}
- Wall reaction A converts instantaneously to its isomer B

The dilute liquid enters in fully developed laminar flow. The question asks for a model and boundary conditions, so no numerical solution is required.

Assumptions

- Steady state.
- Axisymmetric flow and concentration field.

- Constant properties.
- No radial velocity.
- No homogeneous reaction in the liquid.
- Uniform inlet concentration.
- Axial diffusion neglected only when axial convection dominates over the length of interest.

The specified isothermal flow and instantaneous wall reaction are supplied features of the model.

Calculations

Reaction occurs on the wall, so it enters through a boundary condition. It does not supply a volumetric R_A term in the liquid. The steady, axisymmetric form of Eq. 10 is

$$0 = -\frac{1}{r}\frac{\partial (rN_{Ar})}{\partial r} - \frac{\partial N_{Az}}{\partial z}$$

There is no radial convection. Axial convection remains present even though the solute is dilute. The two total-flux components are

$$N_{Ar} = -D_{AB}\frac{\partial c_A}{\partial r}$$

$$N_{Az} = v_z(r)c_A - D_{AB}\frac{\partial c_A}{\partial z}$$

Substituting the fluxes into the balance gives the full convection-diffusion equation,

$$v_z(r)\frac{\partial c_A}{\partial z} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_A}{\partial r}\right) + D_{AB}\frac{\partial^2 c_A}{\partial z^2} \tag{30}$$

For fully developed laminar flow in a circular tube, the velocity profile is

$$v_z(r) = 2\bar{v}\left[1 - \left(\frac{r}{R}\right)^2\right]$$

To judge axial diffusion, compare the convection scale $\bar{v}c_A/L$ with the diffusion scale $D_{AB}c_A/L^2$. Their ratio is the axial Péclet number,

$$\mathrm{Pe}_L = \frac{\bar{v}L}{D_{AB}}$$

For illustration, use $\bar{v} = 0.1\ \mathrm{m\,s^{-1}}$, $L = 0.1\ \mathrm{m}$ and $D_{AB} = 10^{-9}\ \mathrm{m^2\,s^{-1}}$. These are supplementary scale values rather than data supplied in the question. They give

$$\mathrm{Pe}_L = \frac{0.1(0.1)}{10^{-9}} = 10^7$$

Axial convection then dominates axial diffusion over this length, away from axial end regions. The resulting working equation is

$$v_z(r)\frac{\partial c_A}{\partial z} = \frac{D_{AB}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_A}{\partial r}\right) \tag{31}$$

The reduced equation needs inlet data and two radial conditions. The inlet supplies uniform A. Instantaneous reaction holds the catalytic-wall concentration at zero. Centreline symmetry gives zero radial gradient. These conditions form the system

$$\begin{aligned} c_A(r,0) &= c_{A0}, 0 \le r < R \\ c_A(R,z) &= 0, \quad 0 < z \le L \\ \left[\frac{\partial c_A}{\partial r}\right]_{r=0} &= 0, \quad 0 < z \le L \end{aligned}$$

The inlet and wall data are interpreted as one-sided conditions at the inlet-wall corner, where the idealised concentration jumps. Every term in the governing equation has units $\mathrm{kmol\,m^{-3}\,s^{-1}}$.

If axial diffusion is retained in Eq. 30, the axial equation is second order. A finite-domain model then also needs an appropriate outlet condition, such as zero axial concentration gradient at a sufficiently downstream boundary. The Péclet estimate supports the reduced model over a specified scale; it is not a pointwise argument at the wall, where the velocity is zero.

For a finite first-order surface reaction, the wall condition becomes

$$-D_{AB}\frac{\partial c_A}{\partial r} = k_1'' c_A$$

at $r = R$, because diffusive arrival must equal surface consumption.

This formulation is the mass-transfer Graetz problem. In the fully developed concentration region, a constant wall concentration gives $\mathrm{Sh} = k_c d_t / D_{AB} = 3.66$, where $d_t = 2R$ and k_c uses the difference between mixing-cup and wall concentrations. The entrance-region coefficient is larger. The thermal problem with the same geometry and boundary conditions gives $\mathrm{Nu} = 3.66$.

Answer

Use Eq. 31 with

$$v_z = 2\bar{v}\left[1 - \left(\frac{r}{R}\right)^2\right]$$

when axial diffusion can be neglected. Apply uniform inlet concentration, zero A concentration at the catalytic wall, and zero radial concentration gradient at the centreline, as stated above.

If axial diffusion is significant, use Eq. 30 and provide an additional axial boundary condition.

Back to Exercise 3

Exercise 4. Derive a film balance with finite surface reaction

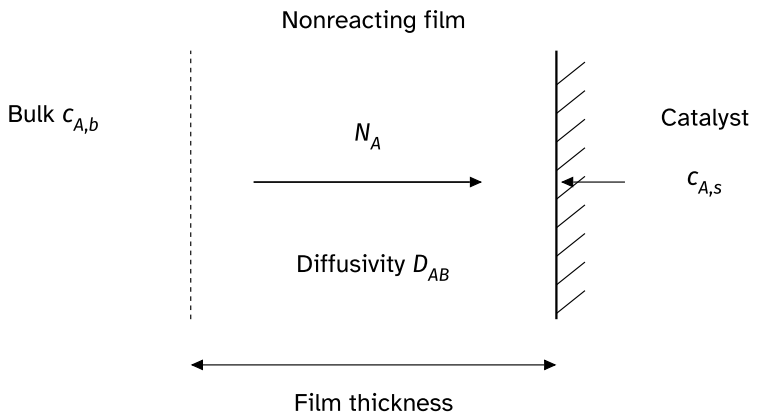


Figure 8: A diffuses from the bulk through a nonreacting film to the catalyst. A finite reaction rate leaves a nonzero surface concentration, determined by matching film transport and surface consumption.

Data

Quantity	Value
Temperature	$T = 500\ \mathrm{K}$
Pressure	$P = 100000\ \mathrm{Pa}$
Bulk mole fraction	$y_{Ab} = 0.020$
Film thickness	$L = 0.0015\ \mathrm{m}$
Diffusivity	$D_{AB} = 6.0 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$
Surface reaction coefficient	$k_s = 0.015\ \mathrm{m\,s^{-1}}$
Surface area	$A_s = 0.040\ \mathrm{m^2}$

Assumptions

- Steady state.
- One-dimensional transport across a plane film.
- Ideal gas behaviour.
- Constant temperature, pressure and diffusivity.
- No gas-phase reaction.
- Negligible normal bulk velocity.

Calculations

For a film slice of area S and thickness Δz, no accumulation or volumetric reaction occurs. The shell balance is

$$S N_A(z) - S N_A(z + \Delta z) = 0 \quad \Rightarrow \quad \frac{dN_A}{dz} = 0$$

With

$$N_A = -D_{AB}\frac{dc_A}{dz}$$

and constant diffusivity, $d^2c_A/dz^2 = 0$. Integrating twice and imposing $c_A(0) = c_{Ab}$ and $c_A(L) = c_{As}$ gives

$$c_A(z) = c_{Ab} + (c_{As} - c_{Ab})\frac{z}{L}, \qquad N_A = \frac{D_{AB}}{L}(c_{Ab} - c_{As})$$

Reaction occurs at the boundary. It is absent from the film differential equation. At steady state delivery equals surface consumption:

$$\frac{D_{AB}}{L}(c_{Ab} - c_{As}) = k_s c_{As}, \qquad c_{As} = \frac{c_{Ab}}{1 + \frac{k_s L}{D_{AB}}}$$

Total gas concentration is uniform, so mole fractions have the same ratio:

$$\frac{k_s L}{D_{AB}} = 0.375$$

$$y_{As} = \frac{0.020}{1.375} = 0.01455$$

$$c = \frac{100000}{8.314(500)} = 24.06\ \text{mol m}^{-3}$$

$$N_A = k_s c y_{As} = 0.015(24.06)(0.01455) = 0.005249\ \text{mol m}^{-2}\,\text{s}^{-1}$$

$$\dot{n}_A = A_s N_A = 0.040(0.005249) = 2.099 \times 10^{-4}\ \text{mol s}^{-1}$$

Both concentration-based resistances have units s m⁻¹: $L/D_{AB} = 25.0$ and $1/k_s = 66.7$. Their sum gives

$$N_A = \frac{c_{Ab}}{\frac{L}{D_{AB}} + \frac{1}{k_s}}.$$

Surface reaction supplies the larger resistance, but neither resistance is negligible.

As $k_s \to 0$, $c_{As} \to c_{Ab}$ and removal tends to zero. As $k_s \to \infty$, $c_{As} \to 0$ and removal approaches the diffusion-limited value $D_{AB}c_{Ab}/L$. The isomerisation exchanges one gas mole for one gas mole, consistent with zero net molar flow. Other stoichiometries require checking that assumption.

For a cylindrical reactor with axial flow, the earlier catalytic-tube example retains axial convection. Its finite-rate wall condition uses the same principle: arriving diffusive flux equals surface consumption. Its radial profile must be found with the axial concentration field, rather than assumed linear as in this plane, nonconvecting film.

Answer

The surface mole fraction is $y_{As} = 0.0146$ and the molar removal rate is $\dot{n}_A = 2.10 \times 10^{-4}\,\mathrm{mol\,s^{-1}}$. Surface reaction supplies the larger resistance, $66.7\,\mathrm{s\,m^{-1}}$, compared with $25.0\,\mathrm{s\,m^{-1}}$ for the film. The slow-reaction limit gives zero removal; the fast-reaction limit gives the diffusion-limited flux $D_{AB}c_{Ab}/L$.

Back to Exercise 4

Exercise 5. Use reaction stoichiometry to determine flux directions

Data

- Surface reaction $R \rightarrow 2P$
- Reactant flux toward the catalyst $N_R = 0.010\,\mathrm{mol\,m^{-2}\,s^{-1}}$
- Comparison reaction $R \rightarrow P$

Positive flux points toward the catalyst.

Assumptions

- Steady surface reaction.
- No surface accumulation.
- Only the stated reaction produces or consumes R and P.

Calculations

Products move away from the surface. Two moles of P leave for each mole of R arriving, so

$$N_P = -2N_R = -2(0.010) = -0.020\,\mathrm{mol\,m^{-2}\,s^{-1}}$$

$$N_R + N_P = 0.010 - 0.020 = -0.010\,\mathrm{mol\,m^{-2}\,s^{-1}}$$

The net molar flow is away from the catalyst, so the equimolar model does not apply. In the total-flux expression

$$N_R = -cD_{RP}\frac{dy_R}{dz} + y_R(N_R + N_P),$$

the bulk term is negative. It opposes R's inward diffusive transport.

The flux relation can also be written $N_R = -N_P/2$. The negative sign expresses opposing directions; the factor comes from stoichiometry.

For $R \rightarrow P$, $N_P = -N_R$ and the total molar flux is zero. That reaction permits the equimolar model under the other stated binary-film assumptions. Constant temperature and pressure alone do not determine the flux ratio.

Answer

For $R \rightarrow 2P$, $N_P = -0.020\,\mathrm{mol\,m^{-2}\,s^{-1}}$ and the total molar flux is $-0.010\,\mathrm{mol\,m^{-2}\,s^{-1}}$, directed away from the catalyst. Equimolar counter-diffusion does not apply. For $R \rightarrow P$, $N_P = -0.010\,\mathrm{mol\,m^{-2}\,s^{-1}}$ and the total molar flux is zero.

Back to Exercise 5

Exercise 6. Distinguish reaction throughout a liquid from reaction at a wall

Data

- Liquid depth $L = 0.010\,\mathrm{m}$
- Fixed top concentration $c_{A0} = 0.25\,\mathrm{mol\,m^{-3}}$
- First-order volumetric rate constant $k_1''' = 0.0020\,\mathrm{s^{-1}}$
- Diffusivity $D_{AB} = 2.0 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$

The bottom is impermeable.

Assumptions

- Steady state.
- One-dimensional diffusion.
- Stationary liquid.
- Dilute oxygen.
- Constant properties.
- First-order homogeneous oxygen consumption.

Calculations

Measure x downwards from the upper surface. Consumption occurs throughout the liquid, so it is a homogeneous reaction and belongs in the local balance:

$$D_{AB}\frac{d^2c_A}{dx^2} - k_1'''c_A = 0, \qquad c_A(0) = c_{A0}, \qquad \left[\frac{dc_A}{dx}\right]_{x=L} = 0$$

The reaction penetration length is

$$\sqrt{\frac{D_{AB}}{k_1'''}} = 0.0010\,\mathrm{m},$$

and

$$\mathrm{Ha} = L\sqrt{\frac{k_1'''}{D_{AB}}} = 10.$$

From Eq. 29,

$$\begin{aligned} N_A(0) &= c_{A0}\sqrt{k_1'''D_{AB}}\tanh(\mathrm{Ha}) \\ &= 0.25\sqrt{0.0020(2.0\times10^{-9})}\tanh(10) \\ &\simeq 5.00\times10^{-7}\,\mathrm{mol\,m^{-2}\,s^{-1}} \end{aligned}$$

Most consumption takes place near the upper surface. Adding more depth has little effect in this large-Ha limit.

With reaction only at a catalytic bottom, the interior has no volumetric source:

$$D_{AB}\frac{d^2c_A}{dx^2} = 0.$$

Replace the impermeable-bottom condition by

$$-D_{AB}c'_A(L) = k_s c_A(L)$$

for a first-order surface reaction. The two rate constants have different units, s^{-1} in the liquid and $m\ s^{-1}$ at the surface.

A pond can require an unsteady absorption model or a steady reaction model. Its size alone does not decide. The stated consumption, flow, initial state and boundary conditions determine which model is appropriate.

Answer

The oxygen influx is $5.00 \times 10^{-7}\ \mathrm{mol\,m^{-2}\,s^{-1}}$ into the liquid. If reaction occurs only at the bottom, use $D_{AB}c''_A = 0$ in the interior and the bottom condition

$$-D_{AB}c'_A(L) = k_s c_A(L).$$

Back to Exercise 6

Exercise 7. An expanding reaction mixture changes the film profile

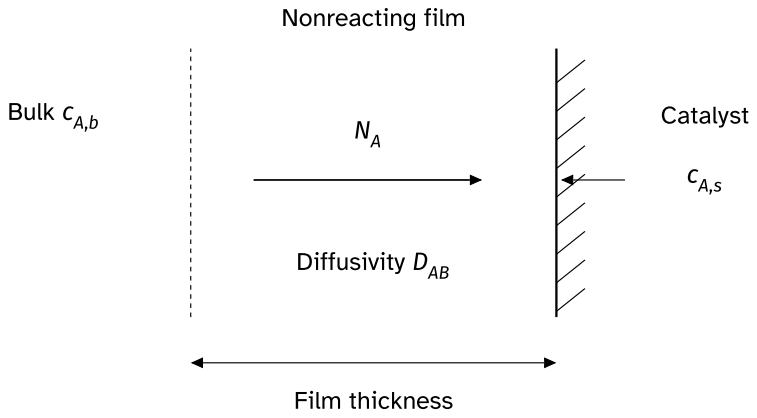


Figure 9: A crosses the gas film toward the catalyst. The surface reaction produces B, whose outward flux changes the mixture molar flow.

Data

Quantity	Value
Film thickness	$\delta = 0.0020\ \mathrm{m}$
Bulk mole fraction	$y_{A0} = 0.20$
Temperature	$T = 500\ \mathrm{K}$
Pressure	$P = 150000\ \mathrm{Pa}$
Diffusivity	$D_{AB} = 2.0 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$
Instantaneous catalyst reaction	$A \rightarrow 3B$

Assumptions

- Steady state.
- One-dimensional transport across a plane film.
- Binary ideal gas mixture.
- Constant temperature, pressure and diffusivity.
- No gas-phase reaction.
- Surface exchange occurs only through the stated reaction.

Calculations

A film shell balance gives $dN_A/dz = 0$ because there is no accumulation or gas-phase reaction. The boundary conditions are $y_A(0) = y_{A0}$ and $y_A(\delta) = 0$. Surface stoichiometry fixes $N_B = -3N_A$, so the total flux is $N_A + N_B = -2N_A$. Product expansion creates outward molar flow even though there is no externally imposed flow through the film.

Keep that flow in the total-flux equation:

$$N_A = -cD_{AB}\frac{dy_A}{dz} - 2y_A N_A$$

$$\frac{dy_A}{1 + 2y_A} = -\frac{N_A}{cD_{AB}}\,dz$$

Integrating from the bulk edge to position z gives

$$\frac{1}{2}\ln\frac{1 + 2y_A(z)}{1 + 2y_{A0}} = -\frac{N_A z}{cD_{AB}}$$

Using the zero surface concentration at $z = \delta$ determines the flux. Substitution back into the integrated equation gives the profile:

$$N_A = \frac{cD_{AB}}{2\delta}\ln(1 + 2y_{A0})$$

$$y_A(z) = \frac{1}{2}\left[(1 + 2y_{A0})^{1-\frac{z}{\delta}} - 1\right]$$

The numerical concentration is $c = P/(RT) = 36.08$ mol m⁻³, so

$$N_A = \frac{36.08(2.0 \times 10^{-5})}{2(0.0020)}\ln[1 + 2(0.20)] = 0.06071\ \mathrm{mol\,m^{-2}\,s^{-1}}$$

An equimolar model would give

$$N_{A,eq} = \frac{cD_{AB}y_{A0}}{\delta} = 0.07217\ \mathrm{mol\,m^{-2}\,s^{-1}}.$$

The actual flux in this film model is 15.9 percent below that value. Outward bulk flow opposes the inward transport of A. This reverses the effect of the inward molar flow in the contracting $2A \rightarrow B$ case above.

At $z = \delta/2$,

$$y_A = \frac{\sqrt{1.4} - 1}{2} = 0.09161,$$

compared with 0.100 for a straight line. The species flux is constant, but its diffusive and bulk contributions vary with composition. Constant flux therefore does not require a linear profile. Both imposed endpoints are recovered exactly. As $y_{A0} \to 0$, the logarithm approaches $2y_{A0}$ and the dilute equimolar estimate is recovered.

Answer

The inward flux is $N_A = 0.0607\ \mathrm{mol\,m^{-2}\,s^{-1}}$, 15.9 percent below the equimolar estimate. The profile is

$$y_A(z) = \frac{1}{2}\left[(1 + 2y_{A0})^{1 - \frac{z}{\delta}} - 1\right].$$

The profile is curved despite the constant species flux.

Back to Exercise 7