Workshop 9: Diffusion with surface reaction

Attempt these problems before opening the worked solutions.

1 Oxidation of a graphite rod

EXERCISE
Exercise 1. Cylindrical diffusion to a shrinking rod

A cylindrical graphite (pure carbon) rod (length = 25 cm, initial diameter = 2 cm) is placed in a combustion chamber with flowing air stream at 1100 K and 2 atm total pressure. A stagnant gas boundary layer 5 mm thick is formed around the surface of the rod. At 1100 K, solid carbon oxidises to carbon dioxide gas,

$$\mathrm{C\ (s)} + \mathrm{O_2\ (g)} \rightarrow \mathrm{CO_2\ (g)}$$

Assuming that the oxidation is limited by molecular diffusion of $\mathrm{O_2}$ through the stagnant gas film, and outside of the gas film, the bulk composition of air stream prevails,

a) Estimate the initial rate of $\mathrm{CO_2}$ production from the rod;

b) Write an equation for the rate of change in the radius of the rod as a function of time.

Data: Density of solid graphite = 2.25 $\mathrm{g/cm^3}$; D_{AB} ($\mathrm{CO_2}$-air) @ 273 K and 1 atm = 0.136 $\mathrm{cm^2/s}$

See solution for Exercise 1

2 Nitric-oxide removal at a catalyst

EXERCISE
Exercise 2. Film resistance and finite surface reaction

Nitric oxide (NO) emission from automobile exhaust can be reduced by using a catalytic converter. The following reaction occurs at the catalytic surface:

$$\mathrm{NO} + \mathrm{CO} \rightarrow 0.5\,\mathrm{N_2} + \mathrm{CO_2}$$

The concentration of NO is reduced by passing the exhaust gases over the surface of the catalyst, and the rate of reduction at the catalyst surface is as follows:

$$N_{NO} = -k'' C_{NO(0)},$$

where $C_{NO(0)}$ is the concentration of NO at the catalyst surface.

As a first approximation, it may be assumed that NO reaches the surface by one-dimensional diffusion through a thin gas film of thickness L that adjoins the surface, and that the effects of bulk motion is negligible. Determine the mole fraction of NO at the catalytic surface and the NO removal rate for a catalytic surface area of 200 cm^2.

Data: The exhaust gas is at $500\,^{\circ}\mathrm{C}$ and 1.2 bar, the mole fraction of NO at L is 0.15, D_{AB} = 10^{-4} m^2/s, k'' = 0.05 m/s and the film thickness is L = 1 mm.

See solution for Exercise 2

Solutions

Exercise solutions

Exercise 1. Cylindrical diffusion to a shrinking rod

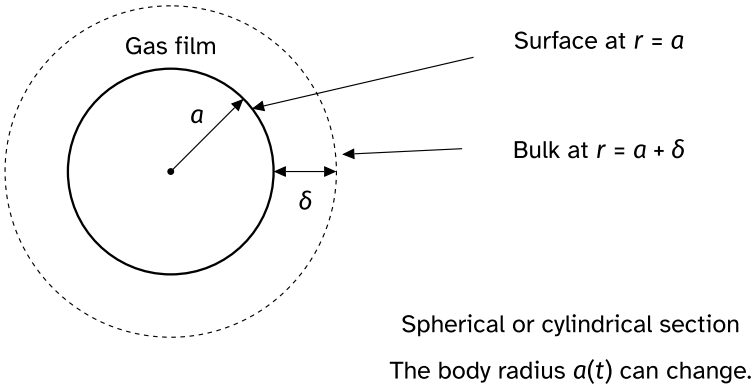


Figure 1: Radial diffusion through a gas film around the graphite rod. The radius a decreases during oxidation, while the film thickness remains fixed. The drawing is a cylindrical cross-section; oxygen diffuses inward and carbon dioxide outward.

Data

Quantity	Symbol	Value
Initial radius and rod length	a_0, ℓ	$0.010, 0.25\ \mathrm{m}$
Gas-film thickness	δ	$0.0050\ \mathrm{m}$
Gas temperature and pressure	T, P	$1100\ \mathrm{K}, 2\ \mathrm{atm}$

Property	Value
Graphite density ρ_C	$2250\ \mathrm{kg\ m^{-3}}$
Carbon molar mass M_C	$0.012\ \mathrm{kg\ mol^{-1}}$
Carbon-dioxide molar mass M_{CO_2}	$0.044\ \mathrm{kg\ mol^{-1}}$
Bulk oxygen mole fraction y_b	0.21
Reference effective gas diffusivity D_0	$0.136\ \mathrm{cm^2\ s^{-1}}$ at 273 K and 1 atm

Assumptions

Treat the source's CO2-air diffusivity as a common effective diffusivity for the oxygen and carbon-dioxide counterdiffusion. This is an approximation to multicomponent air. Nitrogen

has zero net flux, and the reaction exchanges one gas mole for one gas mole, so total gas molar flux is zero. Estimate the diffusivity by

$$D = D_0 \frac{1\,\mathrm{atm}}{P}\left(\frac{T}{273\,\mathrm{K}}\right)^{3/2}.$$

Assume isothermal quasi-steady radial diffusion, no gas-phase reaction, constant density and length, and no transport through the ends. The maintained bulk gas has $y_{O_2}(a+\delta) = y_b$, while the fast reaction gives $y_{O_2}(a) = 0$. Keep δ fixed as a decreases. Derive the constant rN_{O_2} from a cylindrical shell balance, integrate Eq. 1, and relate oxygen consumption to the changing carbon mass. Do not use the initial area as a constant area for the shrinking rod.

Calculations

Use molar flux N_A in $\mathrm{mol\,m^{-2}\,s^{-1}}$ and ideal-gas concentration $c = P/(RT)$, with $R = 8.314\,\mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}}$. With negligible total molar flux, diffusion obeys

$$N_A = -cD\frac{dy_A}{ds}. \tag{1}$$

The coordinate s increases away from the reacting surface. Reactant flux is therefore negative. Report removal and production rates as positive magnitudes.

The oxygen consumption balances carbon-dioxide production mole for mole at the rod surface.

A steady cylindrical shell balance gives

$$\frac{d(rN_{O_2})}{dr} = 0.$$

The positive oxygen consumption rate q satisfies $q = -2\pi r\ell N_{O_2}$.

Integrating Eq. 1 between a and $a+\delta$ gives

$$q(a) = \frac{2\pi\ell cDy_b}{\ln\left(\frac{a+\delta}{a}\right)}. \tag{2}$$

Convert $D_0 = 1.36 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$.

The scaled $D = 5.49989 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$ and $c = 22.1587\,\mathrm{mol\,m^{-3}}$.

At a_0,

$$\ln\left(\frac{a_0+\delta}{a_0}\right) = \ln(1.5) = 0.405465.$$

Using Eq. 2, substitute the length and cylindrical logarithmic factor:

$$q(a_0) = \frac{2\pi(0.25)(22.1587)(5.49989\times10^{-5})(0.21)}{0.405465}$$

Evaluating this expression gives

$$q(a_0) = 9.91479 \times 10^{-4}\,\mathrm{mol\,s^{-1}},$$

$$\dot{m}_{CO_2}(0) = M_{CO_2} q(a_0) = 4.36251 \times 10^{-5}\,\mathrm{kg\,s^{-1}}.$$

The carbon mass is $m_C = \rho_C \pi a^2 \ell$.

Its balance is

$$2\pi\rho_C a\ell \frac{da}{dt} = -M_C q(a).$$

Combining this balance with Eq. 2 yields

$$\frac{da}{dt} = -\frac{M_C c D y_b}{\rho_C a \ln\left(\frac{a+\delta}{a}\right)}, \qquad a(0) = a_0. \tag{3}$$

Initially

$$\frac{da}{dt} = -3.36637 \times 10^{-7}\,\mathrm{m\,s^{-1}}.$$

The negative sign represents loss of radius.

Carbon consumption uses M_C; carbon-dioxide mass production uses M_{CO_2}.

The gas-film diffusion time $\delta^2/D = 0.455\,\mathrm{s}$ is much shorter than the initial shrinkage scale

$$\frac{a_0}{\left|\frac{da}{dt}\right|} = 2.97 \times 10^4\,\mathrm{s},$$

supporting quasi-steady transport initially.

The model excludes combustion heating, carbon-monoxide formation, end effects and changes in the flow as the rod shrinks.

Answer

The initial carbon-dioxide production rate is $9.91 \times 10^{-4}\,\mathrm{mol\,s^{-1}}$, or $4.36 \times 10^{-5}\,\mathrm{kg\,s^{-1}}$. Radius evolves according to Eq. 3, starting from $a_0 = 0.010\,\mathrm{m}$; initially

$$\frac{da}{dt} = -3.37 \times 10^{-7}\,\mathrm{m\,s^{-1}}.$$

Back to Exercise 1

Exercise 2. Film resistance and finite surface reaction

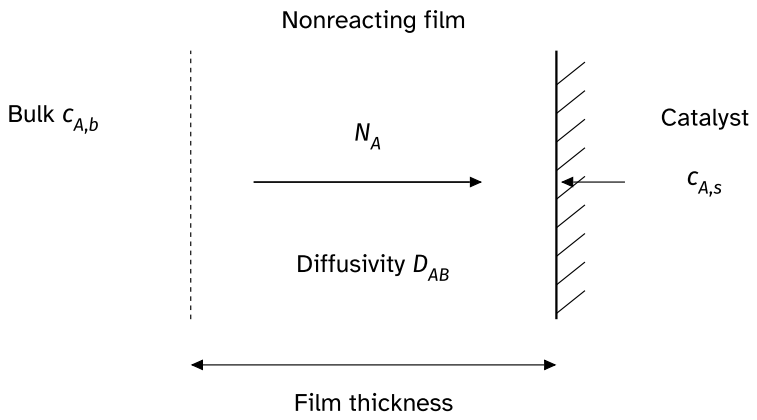


Figure 2: Nitric oxide diffuses through a nonreacting gas film to the catalyst. Its surface concentration is not zero when surface reaction is finite. The solution measures x from the catalyst toward the bulk.

Data

Property	Value
Bulk NO mole fraction y_b	0.15
Film thickness L	$0.0010\,\mathrm{m}$
Effective NO diffusivity D	$1.0 \times 10^{-4}\,\mathrm{m^2\,s^{-1}}$
Surface rate constant k_s	$0.050\,\mathrm{m\,s^{-1}}$
Catalytic area A_s	$200\,\mathrm{cm^2}$
NO molar mass M_{NO}	$0.030\,\mathrm{kg\,mol^{-1}}$

Assumptions

Assume steady isothermal one-dimensional diffusion with constant pressure and D, no gas-phase reaction, sufficient CO, and the source's first approximation of negligible bulk-motion contribution to NO transport. The reaction changes total gas mole number, so this approximation is not exact equimolar diffusion. Do not interpret the 0.15 mole fraction as realistic dilute exhaust data. It is the supplied idealised problem value. At the surface,

$$N_{NO}(0) = -k_s c y_s, \qquad y_s = y_{NO}(0),$$

and $y_{NO}(L) = y_b$. Integrate Eq. 1 in x and equate the film flux to the surface reaction flux.

Calculations

The finite catalytic reaction leaves a nonzero nitric-oxide concentration at the surface.

The steady flux is constant and the profile is linear:

$$y_{NO}(x) = y_s + (y_b - y_s)\frac{x}{L},$$

$$N_{NO} = -\frac{cD}{L}(y_b - y_s).$$

Matching the reaction flux gives

$$\begin{aligned} \frac{D}{L}(y_b - y_s) &= k_s y_s, \\ y_s &= \frac{y_b}{1 + \frac{k_s L}{D}} \\ &= \frac{0.15}{1 + 0.50} = 0.100. \end{aligned} \tag{4}$$

Convert $T = 773.15\,\mathrm{K}$, $P = 120000\,\mathrm{Pa}$ and $A_s = 0.0200\,\mathrm{m}^2$.

Then $c = 18.6684\,\mathrm{mol\,m^{-3}}$ and $N_{NO} = -0.0933421\,\mathrm{mol\,m^{-2}\,s^{-1}}$.

The positive removal rate is

$$\dot{n}_{NO} = -A_s N_{NO} = 1.86684 \times 10^{-3}\,\mathrm{mol\,s^{-1}},$$

$$\dot{m}_{NO} = M_{NO}\dot{n}_{NO} = 5.60052 \times 10^{-5}\,\mathrm{kg\,s^{-1}}.$$

The equivalent concentration-based coefficient is

$$k_{overall} = \left(\frac{L}{D} + \frac{1}{k_s}\right)^{-1}.$$

Its value is $0.0333333\,\mathrm{m\,s^{-1}}$.

The film resistance $L/D = 10\,\mathrm{s\,m^{-1}}$ and reaction resistance $1/k_s = 20\,\mathrm{s\,m^{-1}}$ add.

Reaction supplies twice the film resistance, but neither can be ignored.

The calculated surface fraction in Eq. 4 confirms finite reaction, rather than a perfectly absorbing surface.

These results apply only to the stated film approximation.

Answer

The surface NO mole fraction is 0.100. The positive removal rate is $1.87 \times 10^{-3}\,\mathrm{mol\,s^{-1}}$, equivalent to $5.60 \times 10^{-5}\,\mathrm{kg\,s^{-1}}$, within the stipulated film approximation.

Back to Exercise 2