LECTURE 09

Modeling Mass Transport in Homogeneous Media

Department of Analytical, Colloidal Chemistry and Technology of Rare Elements

Modeling of chemico-technological processes | 6B07102 Chemical Engineering

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Purpose and expected learning outcomes

Purpose: choose the simplest transport equation that is still correct, solve it, and know where it stops being valid.

DISTINGUISH

Diffusion, migration and convection and estimate their time scales.

SOLVE

Steady and transient diffusion problems: membranes, semi-infinite media.

QUANTIFY

When migration can be neglected, using the supporting-electrolyte ratio.

APPLY

Cottrell and microelectrode solutions to measure diffusion coefficients.

CLASSIFY

Regimes with dimensionless groups: Pe for convection, Da for reaction.

DISCRETIZE

Convection–diffusion and recognise non-physical oscillations.

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From transport mechanisms to dimensionless design rules

01 Mechanisms
Diffusion, migration, convection

02 Fick's laws
Steady and transient diffusion

03 Nernst–Planck
Charged species and electroneutrality

04 Analytical solutions
erf, Cottrell, microelectrodes

05 Dimensionless groups
Péclet and Damköhler numbers

06 Numerics
Upwinding and mesh Péclet number

Industrial relevance: membranes • electrochemical cells • corrosion of concrete • drug release • reactors

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Transport mechanisms and time scales

Diffusion, migration and convection are separate fluxes with different time scales.

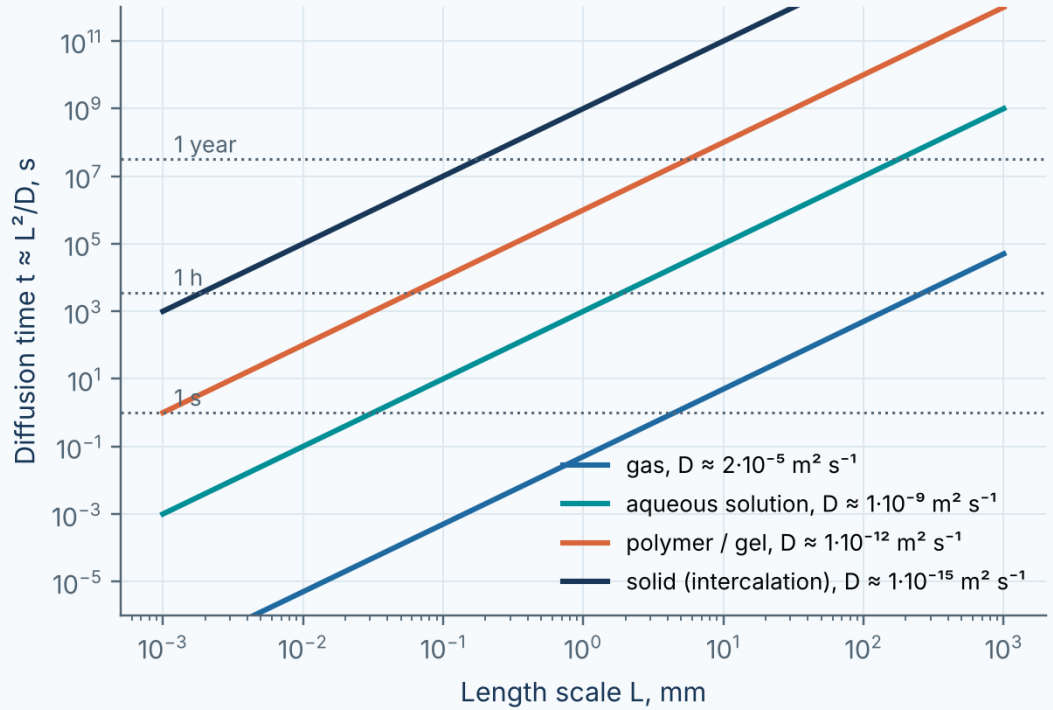
$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi + c_i v$$

$$t_D \approx L^2 / D$$

MODEL CONDITIONS Dilute solution; mobility from the Nernst–Einstein relation $u_i = D_i/RT$; the three fluxes simply add.

EXAMPLE Diffusion across 1 cm takes ~5 s in air but ~28 h in water. Crossing a 10 µm particle with $D = 10^{-15}$ m^2 s^{-1} also takes ~28 h.

EXAMPLE · DIFFUSION TIME $t = L^2/D$



ENGINEERING INTERPRETATION If L^2/D is longer than the process time, transport needs convection or a shorter length scale.

Further reading: Bird, Stewart & Lightfoot, Transport Phenomena, 2nd ed. (2002), ch. 17–19; Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed. (2009); Crank (1975).

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Fick's laws: steady flux and time lag

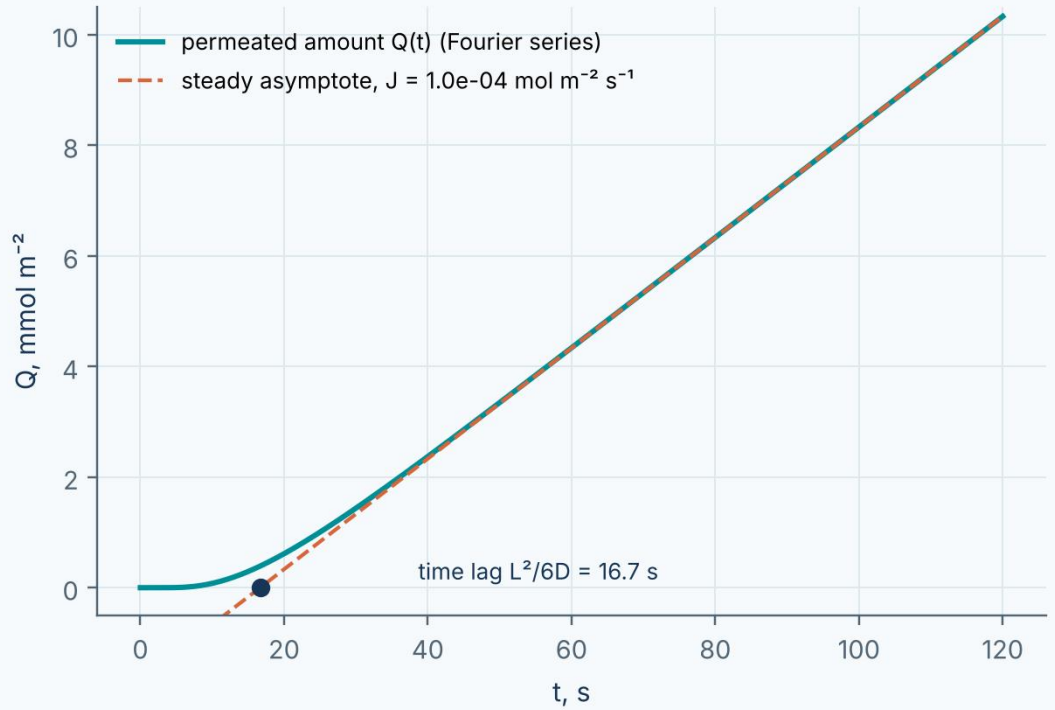
A membrane reaches steady flux only after a characteristic time lag.

$$J = -D\,dc/dx, \quad \partial c/\partial t = D\,\partial^2 c/\partial x^2$$
$$t_{lag} = L^2 / (6D)$$

MODEL CONDITIONS Membrane L = 100 µm, D = 10^{-10} $m^2\,s^{-1}$, upstream c = 100 $mol\,m^{-3}$, downstream ≈ 0, partition coefficient 1.

EXAMPLE Steady flux J = Dc_1/L = $1.0 \cdot 10^{-4}$ $mol\,m^{-2}\,s^{-1}$; time lag 16.7 s. Measuring t_{lag} gives D = $L^2/(6t_{lag})$ without knowing c in the membrane.

EXAMPLE · PERMEATION THROUGH A MEMBRANE



ENGINEERING INTERPRETATION The Daynes–Barrer time-lag method is the standard test for gas permeation through polymer membranes.

Further reading: Bird, Stewart & Lightfoot, Transport Phenomena, 2nd ed. (2002), ch. 17–19; Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed. (2009); Crank (1975).

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Nernst–Planck: when can migration be neglected?

Charged species also move in the electric field of the solution.

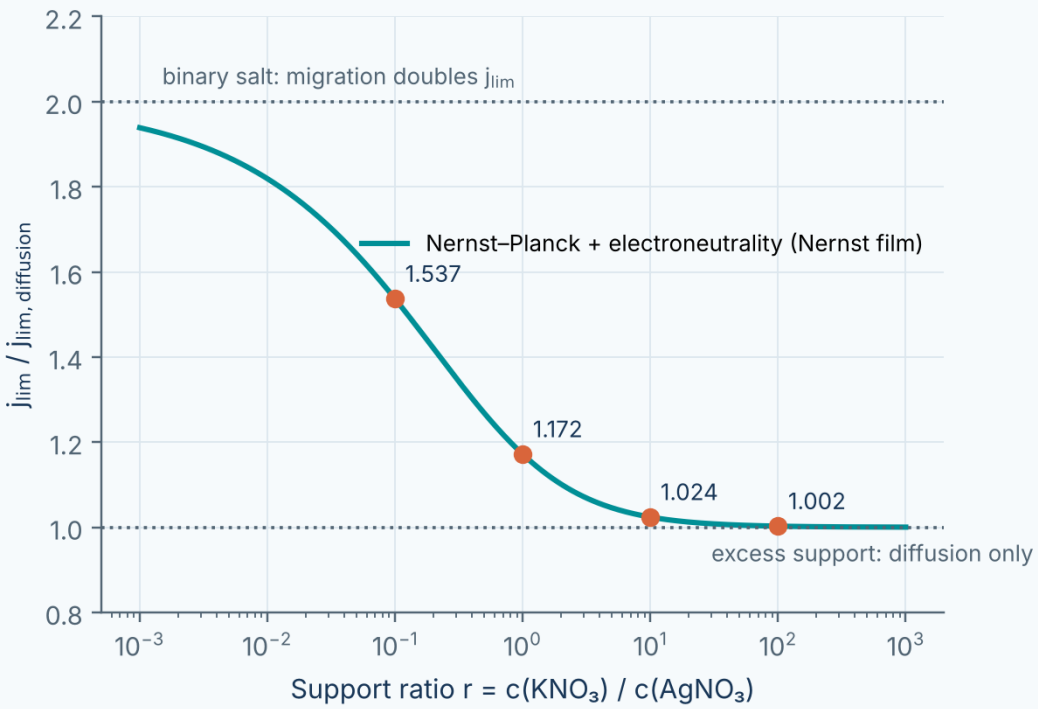
$$N_i = -D_i(\nabla c_i + z_i c_i F \nabla \phi / RT) + c_i v$$

$$\Sigma z_i c_i = 0$$

MODEL CONDITIONS Ag^+ deposition from $AgNO_3$ + KNO_3, steady Nernst film; K^+ and NO_3^- do not react. Analytical result: $j_{lim}/j_{lim,diff} = 2(1+r)[1 - \sqrt{(r/(1+r))}]$.

EXAMPLE No support: migration doubles j_{lim}. r = 1: +17 %; r = 10: +2.4 %; r = 100: +0.25 %.

EXAMPLE · LIMITING CURRENT VS SUPPORT RATIO



ENGINEERING INTERPRETATION With ≥ 50–100-fold supporting electrolyte, migration can be dropped and Fick's law used.

Further reading: Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 11–12; Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 4, 6.

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Semi-infinite diffusion: chloride ingress into concrete

A constant surface concentration produces an erfc profile that spreads as $\sqrt{t}$.

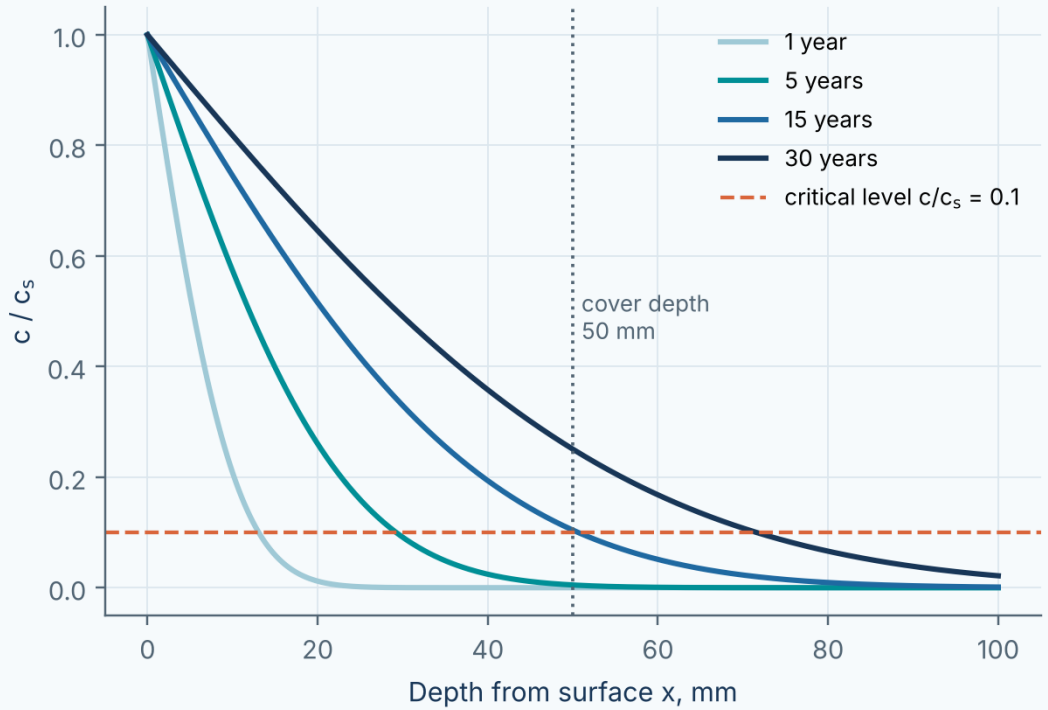
$$c(x,t) = c_s \, \mathrm{erfc}[x / 2(Dt)^{1/2}]$$

$$t_{crit} = (x / 2z)^2 / D$$

MODEL CONDITIONS Apparent $D = 10^{-12}$ m^2 s^{-1} constant, constant surface chloride c_s, no binding; critical level $c/c_s = 0.1$, so $\mathrm{erfc}(z) = 0.1$ and $z = 1.163$.

EXAMPLE With 50 mm cover the critical level reaches the steel after 14.6 years. Doubling the cover to 100 mm gives 4 × 14.6 = 58 years.

EXAMPLE · CHLORIDE PROFILES AFTER 1–30 YEARS



ENGINEERING INTERPRETATION Service life scales with the square of cover depth: the $\sqrt{t}$ law is a design rule, not only a formula.

Further reading: Bird, Stewart & Lightfoot, Transport Phenomena, 2nd ed. (2002), ch. 17–19; Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed. (2009); Crank (1975).

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Transient electrode flux: planar and microelectrodes

A diffusion-limited electrode gives the Cottrell current until radial diffusion takes over.

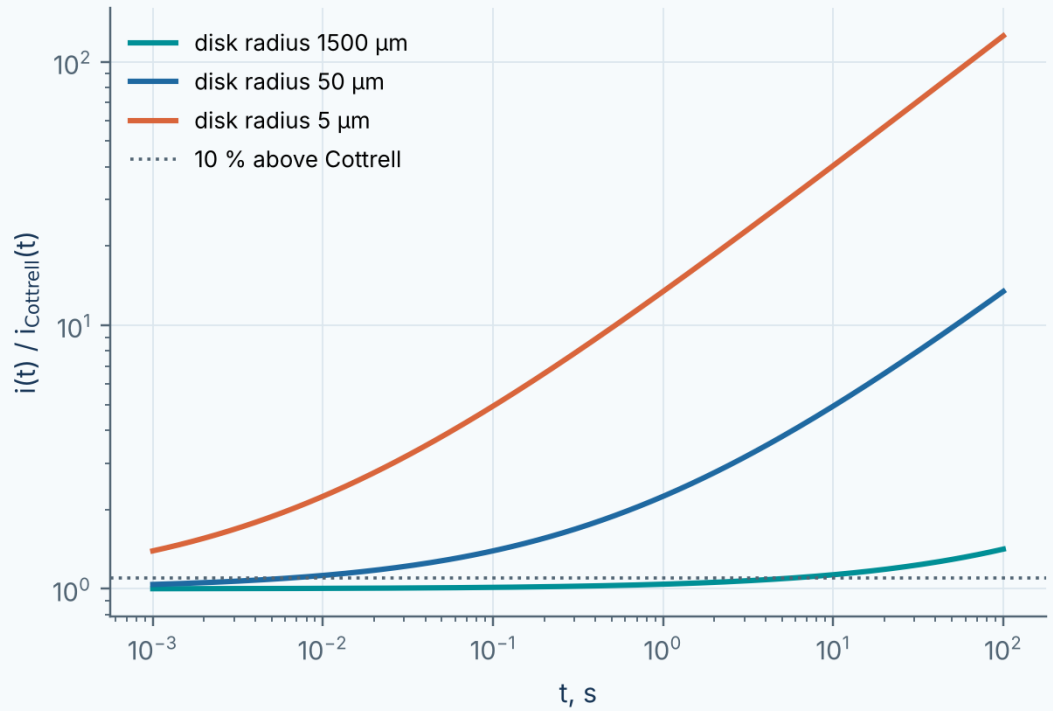
$$i = nFAc_0(D/\pi t)^{1/2}$$

$$i_{ss} = 4nFDc_0r \quad \text{(disk)}$$

MODEL CONDITIONS 5 mM ferricyanide, $D = 7.6 \cdot 10^{-10}$ m^2 s^{-1}, $n = 1$; approximation $i/i_{Cottrell} \approx 1 + 4(\pi Dt)^{1/2}/(\pi r)$.

EXAMPLE 3 mm disk: $i(1\ s) = 53$ µA; planar theory holds within 13 % up to 10 s. For a 5 µm disk the steady term (7.3 nA) dominates after ~10 ms.

EXAMPLE · DEVIATION FROM COTTRELL BEHAVIOUR



ENGINEERING INTERPRETATION Use i vs $t^{-1/2}$ only while $\sqrt{(Dt)} \ll r$ and before natural convection sets in (typically < 10–20 s).

Further reading: Newman & Balsara, Electrochemical Systems, 4th ed. (2021), ch. 11–12; Bard, Faulkner & White, Electrochemical Methods, 3rd ed. (2022), ch. 4, 6.

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Convection–diffusion and the Péclet number

The Péclet number compares transport by flow with transport by diffusion.

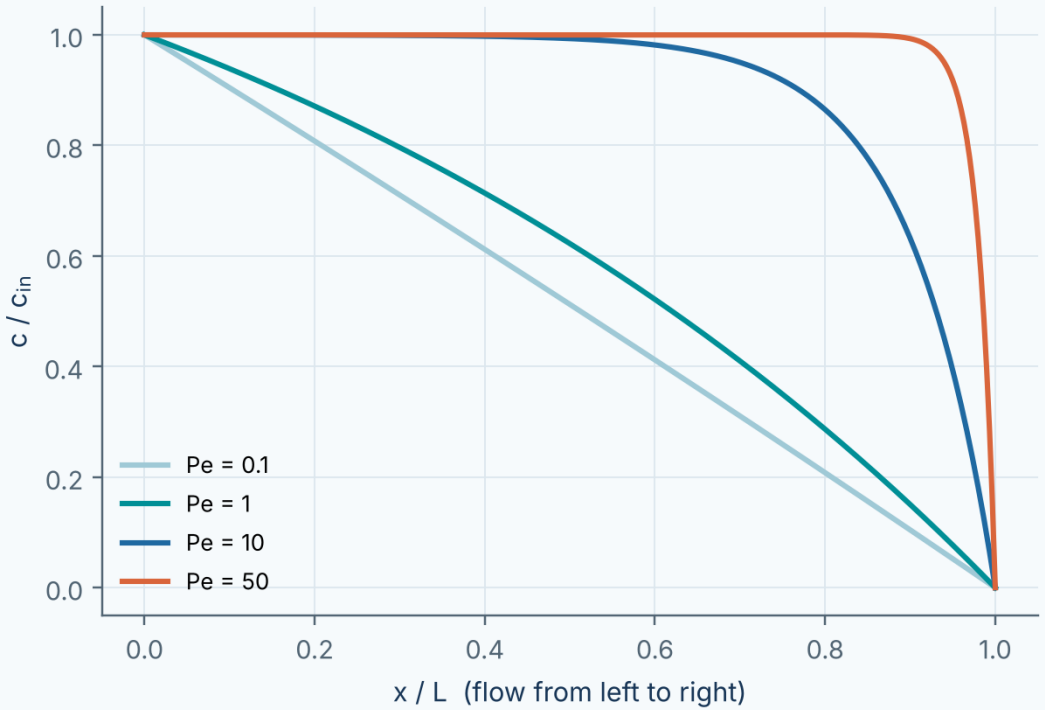
$$v\,dc/dx = D\,d^2c/dx^2$$

$$Pe = vL / D$$

MODEL CONDITIONS Steady 1D, $c(0) = c_{in}$, $c(L) = 0$; flow in +x direction. Analytical solution $c = (e^{Pe \cdot x/L} - e^{Pe})/(1 - e^{Pe})$.

EXAMPLE $v = 1$ mm s^{-1}, $L = 1$ cm, $D = 10^{-9}$ m^2 s^{-1} gives $Pe = 10^4$: diffusion acts only in a layer of order $L/Pe = 1$ µm near the outlet.

EXAMPLE · STEADY PROFILES FOR Pe = 0.1–50



ENGINEERING INTERPRETATION High Pe creates thin concentration boundary layers that the mesh must resolve.

Further reading: Bird, Stewart & Lightfoot, Transport Phenomena, 2nd ed. (2002), ch. 17–19; Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed. (2009); Crank (1975).

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Discretizing convection: upwinding

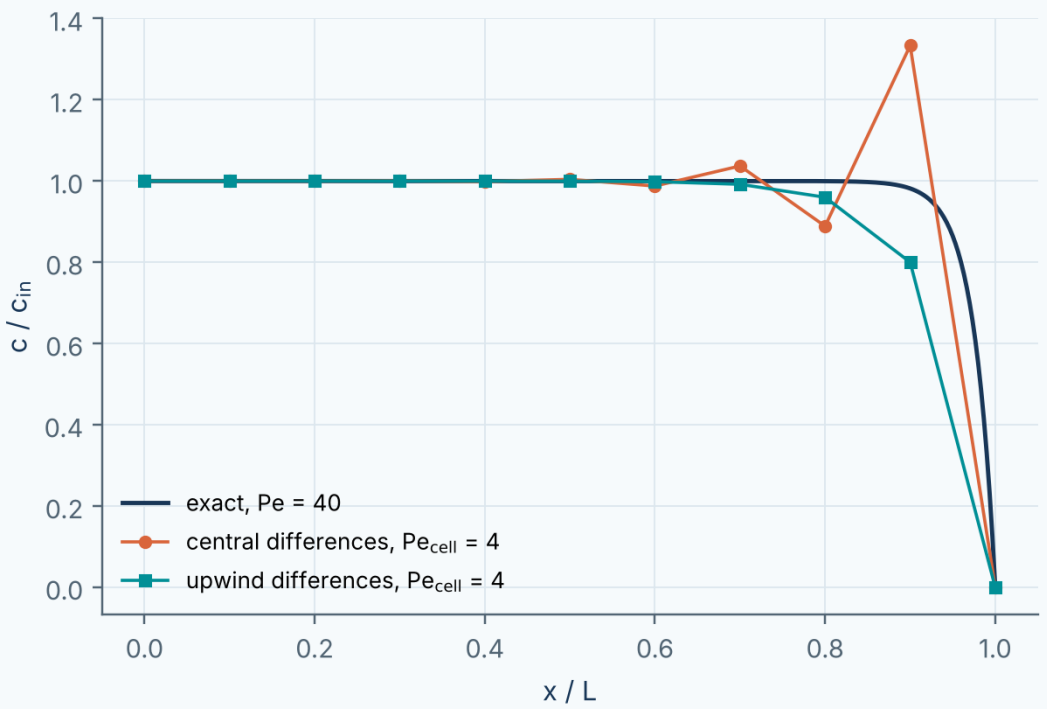
Central differences oscillate when the mesh Péclet number exceeds 2.

$$Pe_h = vh / D \leq 2 \quad \text{(central)}$$
$$\text{upwind: } D_{num} \approx vh / 2$$

MODEL CONDITIONS Same problem as slide 9 with Pe = 40 on 10 elements, so $Pe_h = 4$.

EXAMPLE Central differences give $c = 1.33\, c_{in}$ next to the outlet, a non-physical overshoot. Upwind differences stay bounded but smear the layer by numerical diffusion.

EXAMPLE · CENTRAL VS UPWIND DIFFERENCES



ENGINEERING INTERPRETATION COMSOL applies streamline and crosswind stabilization by default for this reason; refine the mesh as well.

Further reading: Patankar, Numerical Heat Transfer and Fluid Flow (1980), ch. 5; COMSOL Multiphysics Reference Manual (stabilization methods).

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Surface reaction and transport: the Damköhler number

The slower of reaction and transport controls the overall rate.

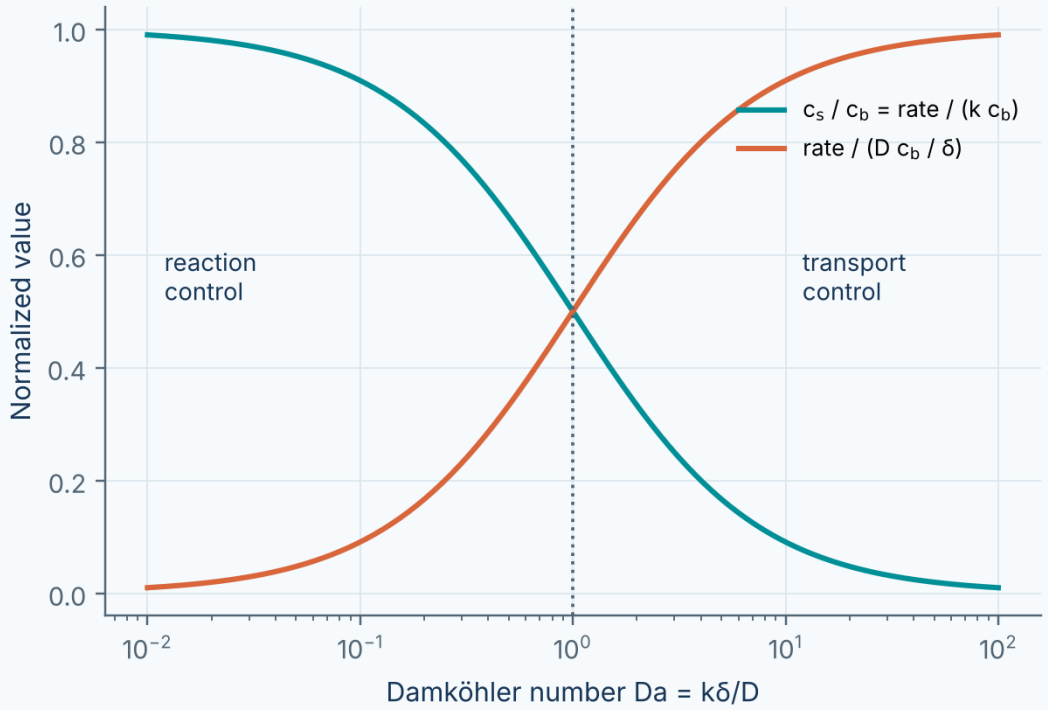
$$k\,c_s = (D/\delta)(c_b - c_s)$$

$$c_s/c_b = 1/(1 + Da),\quad Da = k\delta/D$$

MODEL CONDITIONS First-order surface reaction (k in m s^{-1}) behind a stagnant film of thickness δ, steady state.

EXAMPLE k = 10^{-5} m s^{-1}, δ = 100 µm, D = 10^{-9} m^2 s^{-1} give Da = 1: the rate is half of the kinetic value, and c_s = 0.5 c_b.

EXAMPLE · REACTION- AND TRANSPORT-CONTROLLED REGIMES



ENGINEERING INTERPRETATION Da ≫ 1: stir or thin the film; Da ≪ 1: improve the catalyst. The wrong action brings no gain.

Further reading: Bird, Stewart & Lightfoot, Transport Phenomena, 2nd ed. (2002), ch. 17–19; Cussler, Diffusion: Mass Transfer in Fluid Systems, 3rd ed. (2009); Crank (1975).

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Conclusions: a verified model is a useful model

MECHANISMS

Compare L^2/D, Pe and the support ratio before simplifying the flux.

FICK

Steady flux, time lag and erfc solutions cover most diffusion problems.

MIGRATION

Negligible only with excess supporting electrolyte.

ELECTRODES

Cottrell for planar electrodes; steady currents for microelectrodes.

REGIMES

Pe and Da identify the controlling step and the right design action.

NUMERICS

Keep $Pe_h \leq 2$ or use stabilization; check for overshoots.

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Homework: calculations, interpretation and research

1. THEORY Derive the Nernst–Einstein relation $u_i = D_i/RT$ and show why the migration term vanishes for a neutral species.

2. CALCULATION A time-lag experiment gives $t_{lag} = 45$ s for an 80 µm membrane. Find D. Then find when chloride reaches $c/c_s = 0.1$ at 70 mm cover for $D = 5 \cdot 10^{-13}$ m^2 s^{-1}.

3. CODE Solve steady convection–diffusion for Pe = 5, 20 and 100 on 20 elements with central and upwind schemes. Compare with the exact solution.

4. CRITIQUE List the effects that make a measured i vs $t^{-1/2}$ plot non-linear (convection, edge effects, IR drop, charging) and when each appears.

5. RESEARCH Find two literature values of D for ferricyanide. Explain the differences (temperature, ionic strength, method).

Constants: F = 96485 C mol^{-1}; R = 8.314 J mol^{-1} K^{-1}; T = 298.15 K; erfc(1.163) = 0.10.

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Recommended Literature

1. Fogler, H. S. *Elements of Chemical Reaction Engineering*. 5th ed., Pearson, 2016.
2. Himmelblau, D. M., Riggs, J. B. *Basic Principles and Calculations in Chemical Engineering*. 8th ed., Pearson, 2012.
3. Bird, R. B., Stewart, W. E., Lightfoot, E. N. *Transport Phenomena*. 2nd ed., John Wiley & Sons, 2002.
4. Levenspiel, O. *Chemical Reaction Engineering*. 3rd ed., John Wiley & Sons, 1999.
5. Bequette, B. W. *Process Control: Modeling, Design, and Simulation*. Prentice Hall, 2003.