Chemical and biomedical applications of differential equations

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Outline

- Motivation
- The problems
- Possible use in class: project
- Discussion

Motivation

- Diverse students taking ODEs at KSU
- Wanted more than just standard application problems (e.g. mass-spring, predator-prey, ...)
- No chemical engineering program at KSU, but problems introduce students to some basic ideas

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A related problem on a hydrogel model for knee replacements is included as well (students will use similar mathematical techniques).

Scaffolding

Since this problem is expected to be unfamiliar to most students, plenty of scaffolding and background is provided, starting from:

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A *catalyst* is a material which is capable of accelerating a chemical reaction without being consumed during the reaction process. Catalysts often consist of a porous material with high surface area, in which particles of a precious metal have been dispersed. Catalytic particles are often referred to as pellets. Surrounding each pellet, there is a thin gas film that contains a mix of reactants and products.

Catalyst pellet pictures

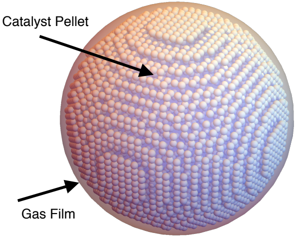

Figure: Catalyst pellet with a thin gas film surrounding it.

Catalyst pellet pictures

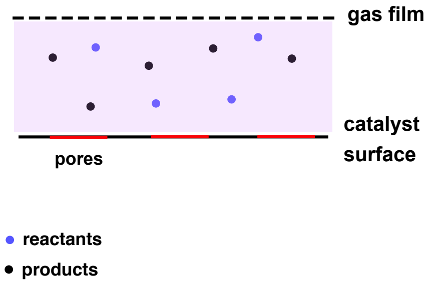

Figure: 2D slice of catalyst surface with reactants and products.

What is a porous medium?

Intuitively, such a medium has “pores", or voids, which are typically filled with a fluid. Examples include sponges, rocks, soil, biological tissues, etc. Imagine something as the figure below.

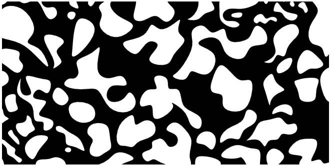

Figure: A porous medium.

Porous media and differential equations: a sidebar

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Let us define:

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If the density of water is assumed to be constant, which we will assume, then the *moisture content* $u(x,t)$ and the *seepage velocity* $q(x,t)$ of the water are governed by the continuity equation

$$\frac{\partial u}{\partial t} + \frac{\partial q}{\partial x} = 0 \tag{1}$$

Porous media and differential equations: a sidebar

as well as Darcy's Law

$$q(x,t) = -K(u)\frac{\partial G}{\partial x} \tag{2}$$

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If chemical and thermal effects are ignored, then for unsaturated flow, G can be expressed as a sum of a gravitational potential and a potential due to capillary suction:

$$G = H(u) + x$$

where $H(u)$ is called a *hydrostatic potential*.

Porous media and differential equations: a sidebar

Combining all of this we obtain the equation

$$\frac{\partial u}{\partial t} = \frac{\partial}{\partial x}\left(K(u)\frac{\partial H}{\partial x}\right) + \frac{\partial}{\partial x}K(u) \tag{3}$$

Empirical expressions are known for $D(u) := K(u)\dfrac{dH}{du}$, and in particular, we have $D(u) = D_0 u^{m-1}$ and $K(u) = K_0 u^n$, for D_0, K_0, m, n positive constants.

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$$\frac{\partial u}{\partial t} = \frac{\partial u^n}{\partial x} + \frac{\partial^2 u^m}{\partial x^2}, \quad n, m \geq 1,\ x \in \mathbb{R},\ t > 0 \tag{4}$$

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Can have students discuss various types of solutions (i.e. traveling waves), but ok, back to the main point...

Reactant diffusion

The reactant must diffuse through the pellet pores to reach the metal atoms that are dispersed through the pellet:

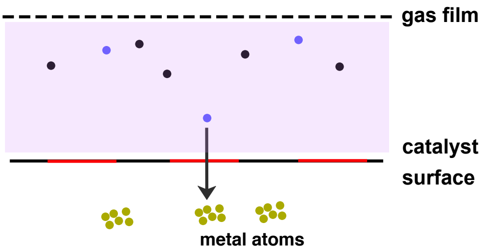

Figure: Reactants must penetrate the pores of the surface in order for the reaction to occur.

Will a reaction occur?

In order for a reaction to occur, the reactant must reach the pellet surface after being transferred through the gas film. Similarly, after the reaction takes place and the product is formed, that product must transfer from the metal back to the pellet surface through the pore, and then out into the reaction medium through the gas film:

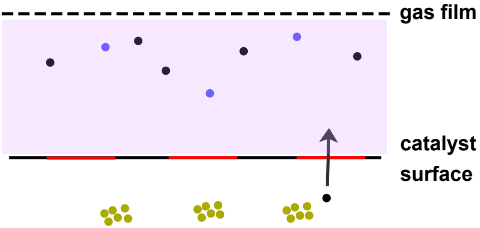

Figure: Products must be transferred back to the surface through the pore.

The model

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Conservation of mass expressed mathematically for c, the concentration of a given chemical, in a spherical pellet with radius r_p gives a second order differential equation:

The main equation

$$D\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dc}{dr}\right)\right) = kR(c), \quad 0 < r < r_p \tag{5}$$

where:

- D is the diffusivity constant, in units of cm^2/s;
- k is the rate constant;
- $R(c)$ is the reaction rate function (could be nonlinear), in units of moles per volume per time (mol/L/s)

The boundary conditions are:

$$\frac{dc}{dr} = 0 \quad \text{at} \quad r = 0,$$

$$c = c_0 \quad \text{at} \quad r = r_p \quad \text{(concentration is fixed at the surface)}$$

Note that the units of k actually depend on the order of the reaction! For example, in a first order reaction, the units of k are $1/s$

Application: catalytic reaction

A useful catalytic chemical reaction is the dehydrogenation of cyclohexane. This industrial process requires the use of $\gamma-$alumina, a porous catalyst pellet with spherical shape. On this sphere, having diameter 5 mm, particles of platinum (a precious and very expensive metal) have been dispersed to catalyze chemical reaction.

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As the name suggests, dehydrogenation involves the removal of hydrogen atoms, a process that usually requires high temperatures. The catalyst γ-alumina is a popular choice of catalyst for this reaction due to its chemical properties, which make it resistant to the extreme reaction conditions.

Dehydrogenation

Below is a depiction of this chemical reaction process. It is a 3 stage process, and in each stage a hydrogen molecule is released.

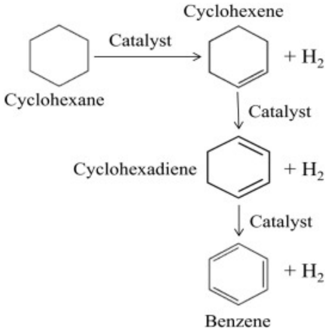

Figure: Dehydrogenation process.

Main question

Suppose that at 700 K, the rate constant for this reaction is $k = 4\ \mathrm{s}^{-1}$ and the diffusivity $D = 5 \times 10^{-2}\mathrm{cm}^2/s$. **Our goal is to calculate the concentration profile of cyclohexane within the pellet.**

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We define the concentration profile as

$$C := \frac{\text{concentration of cyclohexane inside the pellet}}{\text{concentration of cyclohexane at the surface of the pellet}}$$

The differential equation

Mass conservation for cyclohexane gives the following model:

$$\frac{d^2C}{dR^2} + \frac{2}{R}\frac{dC}{dR} = \Phi^2 \frac{R(C)}{c_0}, \quad 0 < R < 1 \tag{6}$$

where R is the re-scaled radial coordinate, i.e $R = r/r_p$. The constant Φ is called the *Thiele modulus* and is given by

$$\Phi = r_p \sqrt{\frac{k}{D}}.$$

This quantity was introduced by E. W. Thiele in 1939 and came to describe the relationship between diffusion and reaction rates in porous catalyst pellets.

Boundary condition

The boundary conditions are:

$$\frac{dC}{dR} = 0 \quad \text{at} \quad R = 0$$

and

$$C = 1 \quad \text{at} \quad R = 1 \quad \text{(this is by definition–we take } c_0 = 1\text{)}$$

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We will assume that $R(c) = kC$ so we have a linear reaction function. With this we will solve (6).

Solving the ODE

Making the substitution $z = CR$ (a hint is useful here) yields the equation

$$\frac{d^2 z}{dR^2} = \Phi^2 z$$

whose solution is

$$z(R) = c_1 e^{\Phi R} + c_2 e^{-\Phi R}$$

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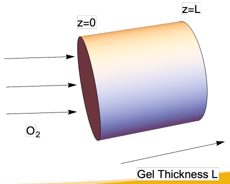
Now we apply the boundary conditions to obtain that

$$C = \frac{z}{R} = \frac{\sinh(\Phi R)}{R \sinh(\Phi)}.$$

Hydrogel model

The equations describing diffusion and reaction in porous catalysts can also be used to derive rates of tissue growth. Over 200,000 patients each year receive knee joint replacements. One approach to growing cartilage to repair damaged knees is to deliver cartilage forming cells in a hydrogel at the damaged area. The design of the gel must be so that the gel can maintain the necessary rates of diffusion of nutrients in the hydrogel. In particular, the gel thickness needs to be designed in such a way so as to allow for rapid transport of oxygen.



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$$\frac{d^2C}{dz^2} = 2\Phi_0, \quad \Phi_0 = \frac{k}{2DC_0}L^2$$

with boundary conditions

$$C(z) = 1 \quad \text{at} \quad z = 0$$

and

$$\frac{dC}{dz} = 0 \quad \text{at} \quad z = 1.$$

Finding C

Integrating the second order equation once yields

$$\frac{dC}{dz} = 2\Phi_0 z + K_1$$

for some constant K_1. The second boundary condition implies that $K_1 = -2\Phi_0$. Integrate the resulting first order equation once more to get

$$C(z) = \Phi_0 z^2 - 2\Phi_0 z + K_2$$

for some constant K_2. Using the other boundary condition, we get $K_2 = 1$, so the concentration profile is

$$C(z) = \Phi_0 z(z-2) + 1 \tag{7}$$

Validity of the solution

Note that the dimensionless concentration profile (7) is only valid for values of $\Phi_0 \leq 1$. Indeed, we can see this by setting $\Phi_0 = 10$ and $z = 0.1$ we find that $C(z) = -0.9$, a negative concentration profile! Thus, mathematically we should actually restrict ourselves to *positive* solutions. Physically, negative concentration values are not useful.

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Can ask further questions using dimensional analysis, e.g. find the rate constant k and calculate the Thiele modulus Φ, etc.

Project implementation

- Assign as group project
- Collect drafts to assess progress
- Provide *detailed* rubric to students
- Have students *grade themselves and their group*
  - Concrete assessments keep students accountable
  - Based on rubrics/group work assessments: Felder, R. M., & Brent, R. (1994). *Cooperative learning in technical courses: Procedures, pitfalls, and payoffs*. Report to the National Science Foundation. (ERIC Document Reproduction Service No. ED 377 038). `http://www.ncsu.edu/felder-public/Papers/Coopreport.html`

Thank you!