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STUDENT VERSION

Chemical and biomedical applications of differential equations

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STATEMENT

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; see Figure 1 and Figure 2 for a 2D version.

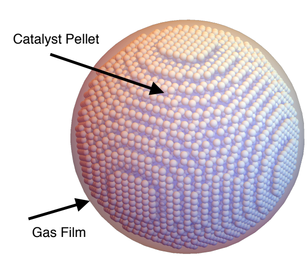

Figure 1. Catalyst pellet with a thin gas film surrounding it.

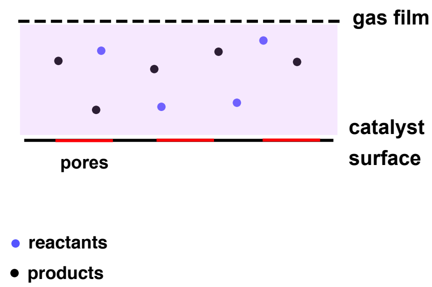

Figure 2. 2D slice of catalyst surface with reactants and products.

First, what does it mean to be porous? Intuitively, such a medium has "pores", or voids, which are typically filled with a fluid. Examples include sponges, rocks, soil, biological tissues, etc. You can imagine something as in Figure 3.

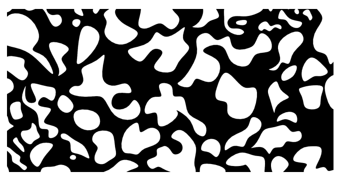

Figure 3. A porous medium.

Then, the reactant must diffuse through the pellet pores to reach the metal atoms that are dispersed through the pellet. See Figure 4.

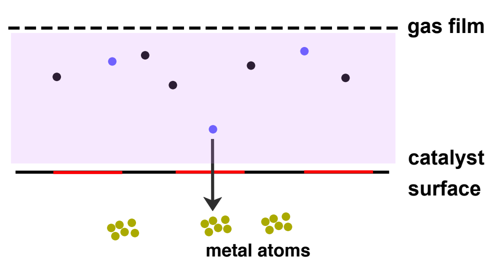

Figure 4. Reactants must penetrate the pores of the surface in order for the reaction to occur.

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. See Figure 5.

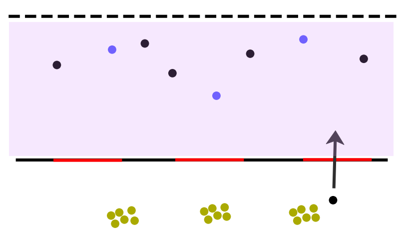

Figure 5. Products must be transferred back to the surface through the pore.

An important problem in chemical engineering is to predict the diffusion and reaction in a porous catalyst pellet. The goal is to predict the overall reaction rate on the catalyst pellet surface [1].

Conservation of mass is a scientific principle stating that in a chemical reaction, matter can neither be created nor destroyed. This can be expressed mathematically for c, the concentration of a given chemical, in a spherical pellet with radius r_p by the following second order differential equation:

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

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:

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

and

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

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 $1/s$.

Question 1.
Define the *effectiveness factor* E as the average reaction rate in the pellet divided by the average reaction rate on the surface:

$$E := \frac{\int_0^{r_p} R(c(r))r^2dr}{\int_0^{r_p} R(c_0)r^2dr}.$$

Integrate the conservation of mass equation (1) to obtain an expression for the effectiveness factor E in terms of $r_p, D, \frac{dc}{dr}, k$, and $R(c_0)$.

Question 2.

Interpret what $E = 1$ and $E < 1$ would mean in terms of the reaction rate in the pellet.

A very useful catalytic chemical reaction is the dehydrogenation of cyclohexane. See Figure 6 for the Lewis structure of cyclohexane (remember your chemistry class?). This industrial process requires the use of $\gamma-$alumina, a porous catalyst pellet with spherical shape (Google it–it's a real thing!). On this sphere, having diameter 5 mm, particles of platinum (a precious and very expensive metal) have been dispersed to catalyze chemical reaction.

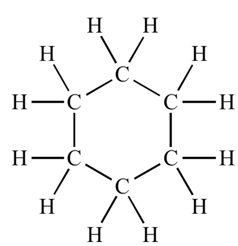

Figure 6. Lewis structure of cyclohexane C_6H_{12}.

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. Figure 7 provides a depiction of this chemical reaction process. It is a 3 stage process, and in each stage a hydrogen molecule is released.

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

The quantity of interest to be calculated is the concentration profile of cyclohexane, which we define as

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

Mass conservation for cyclohexane gives the following model (see [4, Chapter 12] for a full derivation):

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

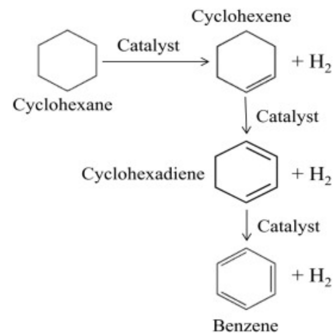

Figure 7. Dehydrogenation process.

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 [5], and came to describe the relationship between diffusion and reaction rates in porous catalyst pellets.

The boundary conditions are similar to the ones stated before, except scaled appropriately:

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

and

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

Question 3.

Suppose $R(c) = kc$, so you have a linear reaction rate function. Use the boundary conditions to solve and provide an explicit solution of (2) . HINT: first make the substitution $z = CR$ and solve the equation satisfied by z.

Question 4.

Using your answer from the previous question, what is the effectiveness factor E just in terms of the Thiele modulus Φ? See Question 1.

Question 5.
Analyze the limit of $C(R)$ as $R \to 0$. Interpret this in terms of the reaction in the center of the pellet. Further, with the value of E that you computed in the last question, what can you say about the average reaction rate in the pellet?

Question 6.
Suppose you have a nonlinear reaction rate now, so that $R(c) = kc^2$. How might you go about computing the concentration profile of cyclohexane and calculating the effectiveness factor in this case?

Question 7.
Explore the catalyst analysis module, adapted from [3]. You will see the relationship between the concentration of the reactant concentration inside the pellet and the pellet radius. What happens as you decrease the pellet radius? What happens if you decrease the rate constant? Why do you think that is?

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[5] E. W. Thiele, *Relation between catalytic activity and size of particle.* Industrial and Engineering Chemistry, 31, 916–920, 1939.