

Gas–solid reaction with porosity change *

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*Dedicated to Alan Lazer
on his 60th birthday*

Abstract

For a gas diffusing through a porous solid and reacting with it isothermally and irreversibly, the mathematical formulation consists of a nonlinear parabolic PDE for the gas concentration coupled with an ODE for the solid concentration. Under the assumption of constant porosity, a fairly complete analysis was provided by Diaz and Stakgold, [3]. Here some of the results are extended to the case when the porosity increases as the solid is consumed. In particular, estimates are given for the time to full conversion of the solid when the reaction rate is proportional to the product of the gas concentration and a fractional power of the solid concentration.

1 Introduction and Preliminary Results

Consider a gas diffusing through a porous solid and reacting irreversibly and isothermally with the solid matrix (or some specified component of it). The solid is being consumed as the reaction proceeds causing an increase in the porosity, that is, the fraction of the volume available to the gas. Although porosity changes have been considered in geophysical problems (see [2], for instance), the methods and results do not seem to apply here. In [3], we dealt with gas–solid reactions while neglecting porosity changes; we established existence and uniqueness as well as various estimates of physical interest. In the present article, we do take into account the porosity changes but we also restrict ourselves to simpler reaction rates, boundary conditions, and initial conditions than in [3]. We assume that the reaction can be regarded as distributed throughout the domain Ω occupied by the porous solid with a rate (per unit volume) proportional to CS^m , where C and S are the nondimensional gas and solid concentrations, respectively. The positive exponent m can be smaller than 1 in some realistic settings: in the Sohn–Szekely model (see [4]) for instance, the porous solid consists of a matrix of very small spherical grains between which the gas diffuses; if

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the reaction is confined to the grain surface and is proportional to its area, then the equivalent distributed reaction rate has $m = 2/3$. An interesting feature of the nonlipschitz case $m < 1$ is that the solid is fully converted in a *finite* time T . One of our principal aims is to provide an estimate for T .

Let us now turn to the formulation of the reaction–diffusion problem in an initially homogeneous porous solid occupying the bounded domain Ω in R^n , when the gas concentration on the boundary $\partial\Omega$ is maintained at a constant positive value. We take the diffusivity as constant but allow the porosity to vary with the solid concentration. After straightforward nondimensionalization and rescaling of the time variable, the mass balances for the solid and gas concentrations yield the system

$$S_t = -S^m C \quad x \in \Omega, \quad t > 0, \quad (1)$$

$$(\epsilon C)_t - \Delta C = -\lambda S^m C (= \lambda S_t) \quad x \in \Omega, \quad t > 0, \quad (2)$$

where the positive constant λ is Thiele's modulus. The porosity ϵ is related to S through

$$\epsilon = \epsilon_0 + \epsilon_1(1 - S), \quad (3)$$

with ϵ_0 and ϵ_1 positive constants. The non-dimensional concentration C and S satisfy the initial and boundary conditions

$$S(x, 0) = 1, \quad C(x, 0) = C_0(x), \quad C(\partial\Omega, t) = 1, \quad (4)$$

where $0 \leq C_0(x) \leq 1$. We seek solutions of (1)–(4) with $S \geq 0$, $C \geq 0$.

A few preliminary remarks are in order:

- a) $S(\cdot, t)$ is decreasing so that ϵ increases with time.
- b) If $S(x_0, t_0) = 0$, then $S(x_0, t) \equiv 0$ for $t \geq t_0$. (A similar result is not necessarily true for C as gas is being supplied through the boundary.)
- c) $0 \leq C(x, t) \leq 1$. This follows from the maximum principle: expanding (2), we obtain the inequality

$$C_t - \frac{1}{\epsilon} \Delta C + \frac{\epsilon_t}{\epsilon} C \leq 0$$

with $\epsilon_t \geq 0$ and $0 < \epsilon_0 \leq \epsilon \leq \epsilon_0 + \epsilon_1$. Thus the coefficient of C is nonnegative and the coefficient of ΔC is a bounded positive function. Hence C obeys a uniform parabolic inequality (see [5]) and its maximum occurs on the parabolic boundary so that $C \leq 1$.

- d) On $\partial\Omega$, $C \equiv 1$ so that (1) becomes an ordinary differential equation for $S(\partial\Omega, t)$ with solution

$$S = B_m(t) = \begin{cases} [1 - (1 - m)t]_+^{1/1-m} & m \neq 1 \\ e^{-t} & m = 1 \end{cases} \quad (5)$$

where z_+ is defined as $\max(0, z)$. For $m \geq 1$, $B_m(t)$ is positive for all t and tends to 0 as $t \rightarrow \infty$; for $m < 1$, $B_m(t)$ decreases until $t = \frac{1}{1-m}$ where it vanishes and remains zero thereafter (note that $B_m(t)$ is continuously differentiable so that it is a classical solution of the differential equation).

At interior points, (1) yields

$$S(x, t) = B_m \left(\int_0^t C(x, \tau) d\tau \right) \quad (6)$$

which could be used to convert (2) into an integro-differential equation for C alone, but we shall not avail ourselves of that formulation. Let us note that if $m \geq 1$, $S(x, t) > 0$ for all x and t . For $m < 1$, full conversion of the solid occurs when the argument of B_m in (6) has reached the value $\frac{1}{1-m}$ for all x ; thus we can characterize the time T to full conversion from

$$\min_{x \in \Omega} \int_0^T C(x, \tau) d\tau = \frac{1}{1-m}. \quad (7)$$

e) The steady state for (1)–(4) is $S \equiv 0$, $C \equiv 1$.

f) We shall not deal here with existence and uniqueness, although the methods of [3] can be adapted for that purpose. We can also show that S and C approach their respective steady states uniformly on $\bar{\Omega}$ as $t \rightarrow \infty$.

2 Upper Bound for the Time T to Full Conversion

Following [6], we introduce the time-integrated difference between the gas concentration and its steady-state value:

$$\eta(x, t) = \int_0^t [1 - C(x, \tau)] d\tau; \quad \eta_t = 1 - C \geq 0. \quad (8)$$

In terms of η , (6) reduces to

$$S = B_m(t - \eta). \quad (9)$$

Integrating (2) with respect to time from 0 to t , we obtain

$$\epsilon \eta_t - \Delta \eta = \epsilon_0(1 - C_0) + (\epsilon_1 + \lambda)(1 - S); \quad \eta(x, 0) = \eta(\partial\Omega, t) = 0. \quad (10)$$

Since ϵ and S are functions of η through (9) and (3), (10) is a scalar PDE for η . In (10), unlike (2), ϵ is not differentiated. From (10) it is clear that $\eta(x, t)$ increases in time to the steady state value

$$\eta_\infty(x) = (\epsilon_1 + \lambda)w(x) + (\epsilon_0)z(x), \quad (11)$$

where w and z satisfy the Poisson equations

$$-\Delta w = 1, \quad x \in \Omega; \quad w(\partial\Omega) = 0 \quad (12)$$

$$-\Delta z = 1 - C_0(x), \quad x \in \Omega; \quad z(\partial\Omega) = 0. \quad (13)$$

We observe that $t - \eta(x, t) = \int_0^t C(x, \tau) d\tau$ is an increasing function of time tending to ∞ as $t \rightarrow \infty$. We can therefore rewrite (7) as

$$\min_{x \in \bar{\Omega}} [T - \eta(x, T)] = \frac{1}{1 - m}, \quad (14)$$

and, hence,

$$T = \frac{1}{1 - m} + \max_{x \in \bar{\Omega}} \eta(x, T) \leq \frac{1}{1 - m} + (\epsilon_0) \|z\| + (\lambda + \epsilon_1) \|w\|, \quad (15)$$

where $\| \cdot \|$ stands for the sup norm.

3 The Pseudo–Steady–State Problem and a Lower Bound for T

The rescaling which occurs in passing from the original mass balances to the nondimensional versions (1) and (2) usually yields $\epsilon \ll 1$. It is therefore common practice among chemical engineers to set $\epsilon = 0$ in (1)–(4). This yields the *pseudo–steady–state (or P.S.S.) problem*

$$\hat{S}_t = -\hat{S}^m \hat{C} \quad x \in \Omega, \quad t > 0 \quad (16)$$

$$-\Delta \hat{C} = -\lambda \hat{S}^m \hat{C} (= \lambda \hat{S}_t) \quad x \in \Omega, \quad t > 0 \quad (17)$$

with initial and boundary conditions

$$\hat{S}(x, 0) = 1, \quad \hat{C}(\partial\Omega, t) = 1. \quad (18)$$

No initial condition can be imposed on \hat{C} since $\hat{C}(x, 0)$ is determined as the solution of the elliptic equation

$$-\Delta \hat{C}(x, 0) = -\lambda \hat{C}(x, 0); \quad \hat{C}(\partial\Omega, 0) = 1. \quad (19)$$

The solution of (19) is unique and positive. As in (8) we introduce

$$\hat{\eta}(x, t) = \int_0^t [1 - \hat{C}(x, \tau)] d\tau, \quad \hat{\eta}_t = 1 - \hat{C} \geq 0 \quad (20)$$

so that

$$\hat{S} = B_m(t - \hat{\eta}). \quad (21)$$

Integrating (17) from time 0 to time t , we obtain

$$-\Delta \hat{\eta} = \lambda(1 - \hat{S}), \quad \hat{\eta}(\partial\Omega, t) = 0. \tag{22}$$

In view of (21), we see that (22) is a scalar elliptic equation for $\hat{\eta}$. It is easy to show that, as $t \rightarrow \infty$, $\hat{S}(x, t)$ decreases monotonically to zero and $\hat{C}(x, t)$ increases monotonically to 1. For $m < 1$, the time \hat{T} to full conversion in the PSS model is characterized by

$$\min_{x \in \bar{\Omega}} [\hat{T} - \hat{\eta}(x, \hat{T})] = \frac{1}{1 - m}.$$

Since $\hat{S} \equiv 0$ for $t \geq \hat{T}$, we see from (22) that $\hat{\eta}(x, \hat{T}) = \lambda w(x)$, where w is defined from (12). Therefore

$$\hat{T} = \frac{1}{1 - m} + \lambda \|w\|, \tag{23}$$

and we have an explicit expression for \hat{T} in terms of the solution of the simple Poisson problem (12) about which much is known (see, for instance, [1]). If, for instance, Ω is a ball of radius a in R^n , then

$$w = \frac{a^2 - |x|^2}{2n} \quad \text{and} \quad \|w\| = \frac{a^2}{2n}.$$

Next, we show that \hat{T} is a lower bound to T if $C_0(x)$ in (4) is smaller than $\hat{C}(x, 0)$ as given by (19). The result will follow easily if we can prove that $\hat{\eta} \leq \eta$. We shall do so by showing that $\hat{\eta}$ is a subsolution to the parabolic problem (10) rewritten as $A\eta = 0$, where

$$A\eta = \epsilon[\eta_t - 1] + \epsilon_0 C_0 - \Delta \eta - \lambda[1 - S] \tag{24}$$

and S, ϵ are regarded as functions of η through (9) and (3).

Since $\hat{\eta}$ satisfies (22) with \hat{S} given by (21), the last two terms on the right side of (24) cancel out for $A\hat{\eta}$. Hence $A\hat{\eta} \leq 0$ if $\hat{\eta}_t \leq 1 - C_0$ or, equivalently, if $C_0(x) \leq \hat{C}(x, t)$. This latter condition holds if

$$C_0(x) \leq \hat{C}(x, 0) \tag{25}$$

because $\hat{C}(x, t)$ is monotonically increasing in time. With $\hat{\eta}$ satisfying the same initial and boundary conditions as η , it follows that $\hat{\eta}$ is a subsolution of (24). Appealing to uniqueness and the theory of monotone operators, we conclude that $\hat{\eta} \leq \eta$. Hence $t - \hat{\eta}(x, t) \geq t - \eta(x, t)$ and since both $t - \hat{\eta}$ and $t - \eta$ are increasing in t , $t - \hat{\eta}$ will reach $\frac{1}{1-m}$ throughout $\bar{\Omega}$ before $t - \eta$. We therefore conclude that, for $C_0(x)$ satisfying (25),

$$\hat{T} \leq T. \tag{26}$$

Combining (26) and (15) we obtain the bounds

$$\hat{T} \leq T \leq \hat{T} + \epsilon_0 \|z\| + \epsilon_1 \|w\| \tag{27}$$

where \hat{T} is given explicitly by (23) and z is the solution of (13). Note that $\|z\| \leq \|w\|$ so that we can replace $\|z\|$ by $\|w\|$ in the upper bound in (27).

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