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# MATHEMATICAL ASPECTS OF THE COMBUSTION OF A SOLID BY A DISTRIBUTED ISOTHERMAL GAS REACTION *

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**Abstract.** When a diffusing gas reacts isothermally with an immobile solid phase, the resulting equations form a semilinear system consisting of a parabolic partial differential equation for the gas concentration coupled with an ordinary differential equation for the solid concentration. Existence and uniqueness proofs are given which include the important case of nonlipschitzian reaction rates such as those of fractional-power type. Various qualitative features of the solution are studied: approach to the steady state; monotonicity in time; and dependence on initial conditions, on the porosity, and on the geometry.

The relationship between the original problem and the pseudo-steady-state approximation of zero porosity is investigated. When the solid reaction rate is nonlipschitzian, there is a conversion front separating a fully converted region adjacent to the boundary and a partially converted interior core. Estimates are given for the time to full conversion. If the gas reaction rate is nonlipschitzian the gas may not at first fully penetrate the solid. Estimates are given for the time at which full penetration occurs.

**Key words.** gas-solid reactions, reaction-diffusion, combustion, pseudo-steady state

**AMS subject classifications.** 35K57, 35R35, 35K50, 35K55

## 1. Introduction and preliminary results.

Many problems of current interest in chemical engineering and metallurgy involve the interactions of diffusing substances with immobile solid phases (see [1] and [16]).

Here we consider the combustion of a porous solid, known as the *pellet*, as it reacts with a gas diffusing through its pores. The reaction, involving only one species of gas and one of solid, is taken to be simple, irreversible, and isothermal. Structural changes during the reaction are neglected. The state variables are the nondimensional concentrations $C$ of the gas and $S$ of the solid. These concentrations are regarded as continuous functions of time $t$ and of a macroscopic position vector $x$. Unlike the "shrinking core" model, the reaction is not confined to a thin surface, but is distributed throughout the solid at a rate proportional to the product of a function of $C$ and of a function of $S$. We assume that the medium can be characterized by effective values of diffusivity and porosity that are independent of position, time, and concentrations. These assumptions can be reconciled with models, such as the Sohn–Szekely model (see [29]), based on a grainlike microstructure for the pellet, with the reaction confined to the surface of the grains.

Mass balances for the solid and gas yield the nondimensional equations

$$S_t = -f(S)g(C) \quad \text{in } (0,\infty)\times\Omega, \tag{1.1}$$

$$\varepsilon C_t - \Delta C = \lambda S_t = -\lambda f(S)g(C) \quad \text{in } (0,\infty)\times\Omega. \tag{1.2}$$

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We are therefore dealing with a semilinear system consisting of a parabolic partial differential equation coupled with an ordinary differential equation. Since (1.2) was obtained by dividing the corresponding dimensional equation by the diffusivity, both $\varepsilon$ and $\lambda$ are inversely proportional to the diffusivity. In the problems of interest here, the porosity $\varepsilon$ falls in the range (0.01, 0.1), and the Thiele modulus $\lambda$ in the range (1, 100). The nondimensional reaction rate $f(S)g(C)$ is only defined for $S \geq 0$ and $C \geq 0$ and vanishes when either $S$ or $C$ vanishes. By nondimensionalization we have also made $f(1) = g(1) = 1$. In applications, it is important to consider cases where $f$ and $g$ are only Hölder continuous but not differentiable at $0+$. For instance, successive reactions in which the intermediate steps have special properties may yield an overall reaction rate which is a fractional power of the concentration of one or both of the reactants. Another example is the Sohn–Szekely grain model which, when translated to our variables, leads to $f(S) = S^{2/3}$ and $f(S) = S^{1/2}$ for three- and two-dimensional problems, respectively. With this in mind, we make the following assumptions on $f$ and $g$:

$$(1.3)\qquad \begin{cases} f \text{ Hölder continuous on } [0,1], f(0) = 0, f(1) = 1; \\ f(S) \text{ positive, monotone increasing for } S > 0; \\ \text{Same conditions on } g \text{ with } C \text{ replacing } S. \end{cases}$$

The special cases $f(S) = S^m, g(C) = C^p$ play a particularly important role in applications. The nonlipschitz cases $m < 1$ and $p < 1$ yield interesting behavior, such as conversion in finite time, dead cores, and moving fronts [10], [13], [28]. The exponents $m$ and $p$ are known as the *orders* of the solid and gas reactions, respectively.

We take $\Omega$ to be a smooth, bounded domain in $R^N$. As initial and boundary conditions associated with (1.1) and (1.2) we choose

$$(1.4)\qquad \begin{aligned} &(a)\, S(0,x) = S_0(x), \quad (b)\, C(0,x) = C_0(x), \qquad x \in \Omega, \\ &(c)\, C + \alpha C_\nu = 1, \qquad x \in \partial\Omega, \quad t > 0. \end{aligned}$$

In the rest of the paper we shall assume, at least, that

$$(H_0)\qquad \begin{aligned} &S_0 \in L^\infty(\Omega), \quad C_0 \in H^2(\Omega) \cap L^\infty(\Omega) \quad \text{and} \quad 0 \leq S_0(x) \leq 1, \\ &0 \leq C_0(x) \leq 1 \quad \text{for a.e. } x \in \Omega. \end{aligned}$$

By nondimensionalization we can choose $\|S_0\| = 1, \|C_0\| \leq 1$, where $\| \ \|$ stands for the sup norm. In (1.4), $\nu$ is the outward normal derivative and $\alpha \geq 0$ is a constant measuring the boundary resistance to mass transfer from the ambient region where the gas concentration is maintained at a uniform value (which has been taken to be unity through nondimensionalization). The special case $\alpha = 0$ leads to a Dirichlet problem.

The problem (1.1)–(1.4) will be referred to as *problem* (P). We seek a solution $(S(t,x), C(t,x))$ with $S \geq 0$ and $C \geq 0$.

Since $\varepsilon$ is small, the term $\varepsilon C_t$ in (1.2) is often neglected in the chemical engineering literature. This changes (1.2) to an elliptic equation for which no initial condition can be imposed. We are thus facing a singular perturbation whose effect cannot be judged a priori. The new problem is known as the *pseudo-steady-state* (p.s.s.) problem, which we denote by $(\hat{\mathrm{P}})$:



$$(1.5)\qquad \hat{S}_t = -f(\hat{S})g(\hat{C}),$$

$$(1.6)\qquad -\Delta\hat{C} = \lambda\hat{S}_t = -\lambda f(\hat{S})g(\hat{C}),$$

$$(1.7)\qquad \hat{S}(0,x) = \hat{S}_0(x) \geq 0, \qquad \|\hat{S}_0\| = 1,$$

$$(1.8)\qquad \hat{C} + \alpha\hat{C}_\nu = 1, \quad x \in \partial\Omega, \quad t > 0.$$

The same nondimensionalization used to obtain (P) gives $(\hat{\mathrm{P}})$. No initial condition is imposed on $\hat{C}$ since $u(x) \doteq \hat{C}(x,0)$ is determined as the unique, necessarily nonnegative, solution of the elliptic problem

$$(1.9)\qquad -\Delta u = -\lambda f(\hat{S}_0)g(u), \quad x \in \Omega; \quad u + \alpha u_\nu = 1, \quad x \in \partial\Omega.$$

In previous papers [25], [27], it has been shown that the solution of $(\hat{\mathrm{P}})$ provides a reasonable approximation to the solution of (P) when $\varepsilon$ is small. Specifically, the following result was obtained for the case $f(S) = S^m$ and $g(C) = C^p$:

$$(1.10)\qquad \int_0^t (\hat{C} - C)\, d\tau \leq \varepsilon\|w\|,$$

where $w(x)$ is the solution of the simple Poisson problem

$$(1.11)\qquad -\Delta w = 1, \quad x \in \Omega; \quad w + \alpha w_\nu = 0, \quad x \in \partial\Omega.$$

For $\alpha = 0$, this is the so-called *torsion* problem about which a great deal of information is available (see, for instance, Bandle [2] and McNabb and Keady [20]). The uniformity of (1.10) in time is perhaps unexpected because $C(0,x)$ and $\hat{C}(0,x)$ are not within $0(\varepsilon)$ of each other. In §3 of the present paper we shall extend (1.10) to general $f$ and $g$ obeying (1.3).

It is of particular interest to know if the solid is fully converted in finite time. We observe from (1.1) that $S(t,.)$ is monotonically decreasing; if for some point $x = \xi$, we have $S(T,\xi) = 0$, then $S(t,\xi) = 0$ for $t \geq T$. This property does not hold for $C$ since diffusion from neighboring points may raise the gas concentration. If $\alpha = 1, S$ on the boundary obeys the ordinary differential equation $S_t = -f(S)$, which can be explicitly integrated. If the integral

$$(1.12)\qquad \int_0^1 \frac{ds}{f(s)} \doteq I$$

is finite (as is the case when $f(S) = S^m$ with $m < 1$) we find that $S$ vanishes on the boundary for $t \geq I$. It then turns out that $S(t,x)$ is identically zero in $\Omega$ for all $t$ sufficiently large. The infimum of such times is the time $t_1$ to full conversion. We shall estimate that time in terms of the corresponding quantity $\hat{t}_1$ for the pseudo-steady-state problem. Section 4 is devoted to this and related questions.

To prove existence of a solution to (P) and $(\hat{\mathrm{P}})$ we first reformulate the problem in §2 by introducing the new variable $X = 1 - S$, which now places the problem in a quasi-monotone framework. A number of authors have used quasi-monotone methods for reaction-diffusion systems (see, for instance, [18] and [22]). Because of the nonlipschitzian character of our nonlinearity and the absence of diffusion in one of the equations, the existence proofs in the literature are not directly applicable to our problem. Our proof is based on a constructive *nonlinear* iteration scheme which preserves qualitative properties at each step.

We first prove existence by the method just described. Continuous dependence and uniqueness are then proved by an $L^1$ technique typical of degenerate quasilinear parabolic problems. Some remarks are made about weakening the regularity assumptions through more abstract approaches. The results in this section were already sketched out in our paper [10].

In §3, we consider the asymptotic behavior of the solution as $t \to \infty$ and the relation between (P) and ($\hat{\mathrm{P}}$) when $\varepsilon$ is small. We show that $S, \hat{S}$ tend monotonically to zero as $t \to \infty$ and that $C, \hat{C}$ tend to 1. The approach to 1 is monotonic for $\hat{C}$ and will be monotonic for $C$ if $C_0$ obeys a certain natural condition. The dependence on $\varepsilon$ is discussed in a number of theorems. If $(S_\varepsilon, C_\varepsilon)$ is the solution of (P) for $\varepsilon > 0$ and $(\hat{S}, \hat{C})$ the solution of ($\hat{\mathrm{P}}$), we show that, under expected conditions on $C_0$ and $S_0$, we have monotonic convergence of $S_\varepsilon$ to $\hat{S}$ and of $C_\varepsilon$ to $\hat{C}$ as $\varepsilon \to 0$. Other theorems in this section deal with the behavior as $\varepsilon \to 0$ of $\int_\Omega |S - S_\varepsilon|\,dx$ and $\int_0^t (\hat{C} - C_\varepsilon)\,d\tau$. These theorems provide a strong generalization of (1.10).

In §4, we discuss the conversion of the solid and, to a lesser extent, the penetration of the gas. For many practical purposes the quantity of interest is the fraction of solid converted up to time $t$,

$$\gamma(t) = 1 - \frac{\int_\Omega S(t,x)\,dx}{\int_\Omega S_0(x)\,dx},$$

with a similar definition for $\hat{\gamma}(t)$. Both of these increase monotonically to 1 as $t \to \infty$. Estimates are given for $\gamma(t)$, particularly in the case of full conversion in finite time ($I$ finite in (1.12)) when the quantities of principal interest are the times $t_1$ and $\hat{t}_1$ to full conversion. Comparison between different types of reaction is also considered.

For certain $g(C)$, for instance if $g(C) = C^p$ with $p < 1$, the gas may not fully penetrate the solid for small $t$. It is easy to see that this "dead core" must disappear in finite time so that $C, \hat{C}$ are strictly positive for $t \geq T$. We obtain estimates for this dead core as well as for $T$.

**2. Existence, uniqueness, and continuous dependence.** In order to use quasi-monotone methods in their simplest form, we begin by replacing $S(t,x)$ by

$$X(t,x) = 1 - S(t,x). \tag{2.1}$$

Since $S(t,\cdot)$ is monotonically decreasing, $X(t,\cdot)$ is monotonically increasing. Note that if $S_0(x) \equiv 1$, as is often the case in applications, then $X$ is the local *fraction of solid* converted by time $t$.

Problem (P), considered on a finite interval $(0,T)$ then becomes the problem (P′):

$$X_t = F(X)g(C) \quad \text{in } Q_T, \tag{2.2}$$
$$\varepsilon C_t - \Delta C = -\lambda F(X)g(C) = -\lambda X_t \quad \text{in } Q_T, \tag{2.3}$$
$$X(0,x) = 1 - S_0(x), \quad C(0,x) = C_0(x) \quad \text{on } \Omega, \tag{2.4}$$
$$C + \alpha C_\nu = 1 \quad \text{on } \Sigma_T, \tag{2.5}$$

where $Q_T = (0,T)\times\Omega, \Sigma_T = (0,T)\times\partial\Omega$, and $F(X) \equiv f(1-X)$ is monotone decreasing in $X$ with $F(0) = 1, F(1) = 0$.

Similar considerations apply to the p.s.s. problem ($\hat{\mathrm{P}}$); see (1.5)–(1.8). Setting $\hat{X} = 1 - \hat{S}$, we obtain problem ($\hat{\mathrm{P}}'$):

$$\hat{X}_t = F(\hat{X})g(\hat{C}) \quad \text{in } Q_T, \tag{2.2a}$$



$$-\Delta\hat{C} = -\lambda F(\hat{X})g(\hat{C}) = -\lambda \hat{X}_t \quad \text{in } Q_T, \tag{2.3a}$$
$$\hat{X}(0,x) = 1 - \hat{S}_0(x) \quad \text{on } \Omega, \tag{2.4a}$$
$$\hat{C} + \alpha\hat{C}_\nu = 1 \quad \text{on } \Sigma_T. \tag{2.4b}$$

If (2.2), (2.3) is regarded as a system for the vector $(X,C)$, the forcing term $(F(X)g(C), -\lambda F(X)g(C))$ is nondecreasing in the off-diagonal variables, i.e., *quasi-monotone.* The system is then in a form which makes it relatively simple to use the notions of sub- and supersolutions.

DEFINITION 2.1. *Let*

$$\overline{X} \in W^{1,\infty}(0,T : L^\infty(\Omega)) \quad \text{and} \quad \bar{C} \in H^1(0,T : L^2(\Omega)) \cap L^2(0,T : H^2(\Omega)) \cap L^\infty((0,T)\times\Omega).$$

*The pair $(\bar{X}, \bar{C})$ is said to be a* supersolution *to* (P′) *if*

$$\begin{aligned}
&\bar{X}_t \geq F(\bar{X})g(\bar{C}) \quad \text{in } Q_T,\\
&\varepsilon\bar{C}_t - \Delta\bar{C} \geq -\lambda F(\bar{X})g(\bar{C}) \quad \text{in } Q_T,\\
&\bar{C} + \alpha\bar{C}_\nu \geq 1 \quad \text{on } \Sigma_T,\\
&\bar{X}(0,x) \geq X_0(x) \doteq 1 - S_0(x) \quad \text{in } \Omega,\\
&\bar{C}(0,x) \geq C_0(x) \quad \text{in } \Omega,
\end{aligned}$$

*at almost every point of the corresponding domain. A* subsolution $(\underline{X}, \underline{C})$ *satisfies the same conditions with all five inequalities reversed. If $(X,C)$ is both a* supersolution *and a subsolution we say that $(X,C)$ is a* solution.

We observe that $(0,0)$ is a subsolution and $(1,1)$ is a supersolution.

Next, we introduce the following iteration scheme: given a pair of smooth functions $(X^{k-1}, C^{k-1}), k \geq 2$, we define the pair $(X^k, C^k)$ as the solution of the *uncoupled nonlinear equations*

$$\begin{aligned}
&X_t^k = F(X^k)g(C^{k-1}) \quad \text{in } Q_T,\\
&X^k(0,x) = X_0(x) \quad \text{in } \Omega,\\
&\varepsilon C_t^k - \Delta C^k = -\lambda F(X^{k-1})g(C^k) \quad \text{in } Q_T,\\
&C^k + \alpha C_\nu^k = 1 \text{ on } \Sigma_T, \quad C^k(0,x) = C_0(x) \quad \text{in } \Omega.
\end{aligned}$$

The existence and uniqueness of the solutions $X^k, C^k$ of these uncoupled problems satisfying

$$X^k \in W^{1,\infty}(0,T : L^\infty(\Omega)) \quad \text{and} \quad C^k \in H^1(0,T : L^2(\Omega)) \cap L^2(0,T : H^2(\Omega)) \cap L^\infty((0,T)\times\Omega)$$

can be found (for instance) in Vrabie [31] (see Theorem 3.10.1).

We are now in a position to prove existence for the equivalent problems (P′) and (P).

THEOREM 2.1. *Assume* (1.3) *and* $(H_0)$. *Let* $X_0 = 1 - S_0$. *Let* $(\underline{X}, \underline{C})$ *be a subsolution and* $(\bar{X}, \bar{C})$ *a supersolution with* $(\underline{X}, \underline{C}) \leq (\bar{X}, \bar{C})$. *Then there exists a solution* $(X,C)$ *of* (P′) *satisfying* $(\underline{X}, \underline{C}) \leq (X,C) \leq (\bar{X}, \bar{C})$.

*Proof.* Consider the sequences $(\underline{X}^k, \underline{C}^k)$ and $(\bar{X}^k, \bar{C}^k)$ obtained by applying our iteration scheme to $(\underline{X}^1, \underline{C}^1) = (\underline{X}, \underline{C})$ and $(\bar{X}^1, \bar{C}^1) = (\bar{X}, \bar{C})$, respectively. By repeated application of the comparison principle for the uncoupled equations, we see that the sequence $(\underline{X}^k, \underline{C}^k)$ is monotonically increasing while $(\bar{X}^k, \bar{C}^k)$ is monotonically decreasing. From the hypothesis $(\underline{X}, \underline{C}) \leq (\bar{X}, \bar{C})$ we can also show that $(\underline{X}^k, \underline{C}^k) \leq (\bar{X}^k, \bar{C}^k)$. The monotonically increasing sequence $(\underline{X}^k, \underline{C}^k)$ is bounded above and must therefore converge as stated to $(\underline{X}, \underline{C})$. To show that $(\underline{X}, \underline{C})$ is a solution it is enough to use the following a priori estimates:

$$\|\underline{X}_t^k\|_{L^\infty((0,T)\times\Omega)} \leq 1,$$
$$\|\varepsilon \underline{C}_T^k\|_{L^2(0,T:L^2(\Omega))} \leq \|\lambda F(\underline{X}^{k-1}) g(\underline{C}^k)\|_{L^2(0,T:L^2(\Omega))} + \|C_0\|_{H^1(\Omega)}^{1/2} \leq M(T,\Omega)$$

for some constant $M(T,\Omega) > 0$ independent of $k$ (this follows from a well-known result due to Brezis; see Theorem 1.9.3 in Vrabie [31]); and

$$\|\Delta \underline{C}^k\|_{L^2(0,T:L^2(\Omega))} \leq M(T,\Omega) + |\Omega|^{1/2}.$$

Standard arguments show that $(\underline{X}, \underline{C})$ is a solution with the regularity mentioned in Definition 2.1. Similarly $(\bar{X}^k, \bar{C}^k)$ converges downwards to a solution $(\bar{X}, \bar{C})$; clearly $(\bar{X}, \bar{C}) \geq (\underline{X}, \underline{C})$. □

*Remark* 2.1. Under the additional assumptions

$$C_0 \in C^{2+\delta}(\Omega) \quad \text{and} \quad S_0 \in C^\delta(\Omega),$$

it is possible to show that the functions $(\underline{X}, \underline{C}), (\bar{X}, \bar{C})$ obtained in Theorem 2.1 are, in fact, classical solutions. Indeed, we point out first that the (unique) solutions $(X^k, C^k)$ of the uncoupled problems are classical solutions as follows from an existence result due to Pao [21]. In order to show that the limit $(\underline{X}, \underline{C})$ is a classical solution we can proceed as follows: since $\varepsilon(\underline{C}_t - \Delta \underline{C}) \in L^\infty((0,T)\times\Omega)$ we deduce by well-known regularity results (see, e.g., references in [15]) that $\underline{C} \in C^\mu([0,T]\times\bar{\Omega})$. Thus $g(\underline{C})$ is a Hölder continuous function. Using the explicit formula (4.4) for $\underline{X}$ we conclude that $\underline{X}$, and hence $F(\underline{X})$, is a Hölder continuous function. Finally, from the equation, $\varepsilon(\underline{C}_t - \Delta\underline{C})$ is a Hölder continuous function, which implies that $\underline{C} \in C^{1,2}_{t,x}((0,T)\times\bar{\Omega}) \cap C^0([0,T]\times\bar{\Omega})$ and satisfies the equation in the classical sense.

*Remark* 2.2. The existence of solutions for the coupled system can also be obtained by means of fixed point arguments using the compactness of some suitable "Green operator." This approach is developed in the article by Diaz and Vrabie [11], where the case of $f$ and $g$ discontinuous at the origin is also considered.

The existence proof of Theorem 2.1 constructs two solutions $(\underline{X}, \underline{C})$ and $(\bar{X}, \bar{C})$. The following theorem, using an $L^1$ technique typical of some degenerate quasilinear parabolic equations, proves continuous dependence and uniqueness for a general class of solutions (including the ones obtained in Theorem 2.1).

THEOREM 2.2. *Let $f$ and $g$ be continuous nondecreasing functions with $f(0) = g(0) = 0$. Let $(S,C), (S^*,C^*)$ be solutions of* (P) *(in the sense of Definition* 2.1*) corresponding to the initial data $(S_0,C_0), (S_0^*,C_0^*)$. Then for any $t \geq 0$ we have that*

$$\begin{aligned} \varepsilon \int_\Omega |C(t,x) - C^*(t,x)|\,dx + \lambda \int_\Omega |S(t,x) - S^*(t,x)|\,dx \\ + \frac{1}{\alpha}\int_0^t \int_{\partial\Omega} |C(\tau,\sigma) - C^*(\tau,\sigma)|\,d\tau\,d\sigma \\ \leq \varepsilon \int_\Omega |C_0(x) - C_0^*(x)|\,dx + \lambda \int_\Omega |S_0(x) - S_0^*(x)|\,dx. \end{aligned} \tag{2.6}$$



*In particular, a solution $(S,C)$ (in the sense of Definition* 2.1*) is unique.*

*Proof.* We start by assuming $f$ and $g$ strictly increasing. We have that

$$(S - S^*)_t + (f(S) - f(S^*))g(C^*) = -f(S)(g(C) - g(C^*)), \tag{2.7}$$

$$\varepsilon(C - C^*)_t - \Delta(C - C^*) + \lambda f(S)(g(C) - g(C^*)) = -\lambda(f(S) - f(S^*))g(C^*). \tag{2.8}$$

Now, multiplying (2.7) by sign $(S - S^*)$ and using

$$\int_0^t \int_\Omega h_t(\tau,x)\,\mathrm{sign}\,(h(\tau,x))\,dx\,d\tau = \int_\Omega |h(t,x)|\,dx - \int_\Omega |h(0,x)|\,dx \tag{2.9}$$

for any $h \in W^{1,1}(0,T : L^1(\Omega))$, we have that

$$\begin{aligned} \int_\Omega |S(t,x) - S^*(t,x)|\,dx + \int_0^t \int_\Omega g(C^*)|f(S) - f(S^*)|\,dx\,d\tau \\ \leq \int_\Omega |S_0(x) - S_0^*(x)|\,dx + \int_0^t \int_\Omega f(S)|g(C) - g(C^*)|\,dx\,d\tau, \end{aligned} \tag{2.10}$$

where we have used the fact that $f(S) \geq 0$ if $S \geq 0, g(C) \geq 0$ if $C \geq 0, \mathrm{sign}(S - S^*) = \mathrm{sign}(f(S) - f(S^*))$, and $(f(S) - f(S^*))\mathrm{sign}(f(S) - f(S^*)) = |f(S) - f(S^*)|$. Analogously multiplying (2.8) by $\mathrm{sign}(C - C^*)$ and using the fact that

$$-\int_\Omega \Delta(C - C^*)\mathrm{sign}(C - C^*)\,dx \geq \frac{1}{\alpha}\int_{\partial\Omega} |C - C^*|\,d\sigma, \tag{2.11}$$

we conclude (as before) that

$$\begin{aligned} \varepsilon \int_\Omega |C(t,x) - C^*(t,x)|\,dx + \frac{1}{\alpha}\int_0^t \int_{\partial\Omega} |C - C^*|\,d\sigma \\ + \lambda \int_0^t \int_\Omega f(S)|g(C) - g(C^*)|\,dx\,d\tau \\ \leq \varepsilon \int_\Omega |C_0(x) - C_0^*(x)|\,dx + \lambda \int_0^t \int_\Omega |f(S) - f(S^*)|g(C^*)\,dx\,d\tau. \end{aligned} \tag{2.12}$$

Multiplying (2.10) by $\lambda$ and adding the result to (2.12) we obtain the conclusion (2.6). Inequalities (2.9) and (2.11) are justified as usual in the $L^1$ theory of evolution equations by regularizing the sign function. Finally, if $f$ and $g$ are not strictly increasing functions we approximate them by strictly increasing functions and pass to the limit. □

Note that in the case of $\alpha = 0$, the boundary term is absent in (2.6).

For the case of the pseudo-steady-state problem we have the following theorem.

THEOREM 2.3. *Let $f$ and $g$ be continuous nondecreasing functions with $f(0) = g(0) = 0$. Then the problem* ($\hat{\mathrm{P}}$) *has a unique solution $(\hat{S}, \hat{C})$.*

*Proof.* By the same arguments as in Theorem 2.2 we deduce that if $(\hat{S}, \hat{C})$ and $(\hat{S}^*, \hat{C}^*)$ are two solutions then

$$\begin{aligned} \lambda \int_\Omega |\hat{S}(t,x) - \hat{S}^*(t,x)|\,dx + \frac{1}{\alpha}\int_0^t \int_{\partial\Omega} |\hat{C}(\tau,\sigma) - \hat{C}^*(\tau,\sigma)|\,d\sigma d\tau \\ \leq \lambda \int_\Omega |\hat{S}(0,x) - \hat{S}^*(0,x)|\,dx. \end{aligned}$$

In particular, as $\hat{S}(0,x) = \hat{S}^*(0,x)$ we conclude that $\hat{S} \equiv \hat{S}^*$ and that $\hat{C}$ and $\hat{C}^*$ are solutions of the elliptic problem

$$-\Delta u + B_t(x,u) = 0 \quad \text{in } \Omega,$$
$$\alpha \frac{\partial u}{\partial \nu} + u = 1 \quad \text{on } \partial\Omega,$$

where $B_t(x,r) = f(\hat{S}(t,x))g(r)$ for any $r \in \mathbb{R}, x \in \Omega$, and $t \in (0,T)$ (here $t$ is a parameter). The uniqueness of $u = \hat{S} = \hat{S}^*$ is now a well-known result since $B$ is monotone nondecreasing in $r$. □

*Remark* 2.3. Theorem 2.2 improves a previous result due to Pao [22] where the nonlinearities are assumed to be Lipschitz continuous. Some papers where an $L^1$ technique is used for parabolic systems are [6], [15], and [33].

*Remark* 2.4. Basing themselves on our earlier paper [10], DiLiddo and Maddalena were able to prove existence for a different type of problem arising in chemical engineering [12].

## 3. Asymptotic behavior and monotonicity.

**3.1. Monotonicity in $\lambda$ and initial data.** Monotone behavior of the solution of (P′) with respect to initial data and with respect to $\lambda$ are easy to prove. Monotonicity in time and with respect to $\varepsilon$ will require a condition on $C_0(x)$.

PROPERTY I. *For fixed $\lambda$ and $\varepsilon$, the solutions of* (P′) *are ordered according to their initial values: if $(X_0^{(1)}, C_0^{(1)}) \le (X_0^{(2)}, C_0^{(2)})$ then the respective solutions of* (P′) *satisfy*

$$(X^{(1)}(t,x), C^{(1)}(t,x)) \le (X^{(2)}(t,x), C^{(2)}(t,x)) \quad \textit{for all } x, t.$$

The result follows from the observation that $(X^{(2)}(t,x), C^{(2)}(t,x))$ is a supersolution of problem (P′) with initial data $(X_0^{(1)}, C_0^{(1)})$.

PROPERTY II. *For fixed $\varepsilon$ and initial data, the solutions of* (P′) *are ordered inversely with $\lambda$:*

$$\lambda_1 \ge \lambda_2 \Rightarrow (X^{(1)}(t,x), C^{(1)}(t,x)) \le (X^{(2)}(t,x), C^{(2)}(t,x)).$$

Again, the proof consists of noting that $(X^{(2)}, C^{(2)})$ is a supersolution of (P′) with $\lambda = \lambda_1$.

Monotonicity with respect to $t$ is a bit more subtle. It is obvious from (2.2) that $X(t,\cdot)$ is monotonically increasing. Since $C_0(x) \le 1$ and the steady state is $C_\infty(x) = 1$, we can only hope to show that $C(t,\cdot)$ is monotonically increasing, but, unfortunately, this cannot be true for all $C_0(x)$. Indeed at $t = 0, C_t \ge 0$ only if

$$-\Delta C_0 + \lambda f(S_0(x))C_0(x) \le 0. \tag{3.1}$$

Rather than (3.1) we prefer to use the condition

$$-\Delta C_0 + \lambda C_0(x) \le 0, \qquad x \in \Omega, \tag{3.2}$$

which clearly implies (3.1). We also need a condition on the boundary values of $C_0(x)$:

$$C_0 + C_{0,\nu} - 1 \le 0, \qquad x \in \partial\Omega. \tag{3.3}$$

We can then conclude with the following property (see Theorem 3.1).



PROPERTY III. *If $C_0(x)$ satisfies* (3.2) *and* (3.3), *then $t \to (X(t,x), C(t,x))$ is monotone increasing for each $x$.*

We shall also show (see Lemma 3.1) that under the same conditions on $C_0(x)$ we have monotone behavior with respect to $\varepsilon$. As expected on physical grounds, $(X, C)$ increases as $\varepsilon$ decreases.

PROPERTY IV. *For fixed $\lambda$ and initial data, suppose that $\varepsilon_1 > \varepsilon_2 > 0$ and $C_0(x)$ satisfies* (3.2) *and* (3.3); *then the respective solutions of* (P′) *are ordered so that*

$$(X^1(t,x), C^1(t,x)) \le (X^2(t,x), C^2(t,x)) \quad \textit{for all } (t,x).$$

For the pseudo-steady-state problem only the initial value $\hat{X}_0$ is at our disposal since the initial value $\hat{C}_0$ of the gas concentration is determined from $\hat{X}_0(x)$ as the solution of the elliptic problem

$$\begin{aligned} &-\Delta \hat{C}_0(x) + \lambda F(\hat{X}_0)g(\hat{C}_0) = 0, \qquad x \in \Omega,\\ &\hat{C}_0 + \hat{C}_{0,\nu} = 1, \qquad x \in \partial\Omega. \end{aligned} \tag{3.4}$$

The following results are then easily obtained.

PROPERTY I*. *For fixed $\lambda$, the solutions of* $(\hat{\mathrm{P}}')$ *are ordered according to the initial values of $\hat{X}$: if $\hat{X}_0^{(1)} \le \hat{X}_0^{(2)}$, then*

$$\hat{C}_0^{(1)} \le \hat{C}_0^{(2)} \quad \textit{and} \quad (\hat{X}^{(1)}(t,x), \hat{C}^{(1)}(t,x)) \le (\hat{X}^{(2)}(t,x), \hat{C}^{(2)}(t,x)) \quad \textit{for all } (t,x).$$

This follows from the maximum principle or by observing that $\hat{C}_0^{(1)}$ is a subsolution to the scalar elliptic problem for $\hat{C}_0^{(2)}$.

PROPERTY II*. *For fixed initial $\hat{X}_0$, the solutions of* $(\hat{\mathrm{P}}')$ *are ordered inversely with $\lambda$:*

$$\lambda_1 \ge \lambda_2 \Rightarrow (\hat{X}^{(1)}, \hat{C}^{(1)}) \le (\hat{X}^{(2)}, \hat{C}^{(2)}) \quad \textit{for all } (t,x).$$

Monotonicity with time is now automatic (see Theorem 3.2).

PROPERTY III*. *$t \to (\hat{X}(t,x), \hat{C}(t,x))$ is monotone increasing for all $x$.*

In this section we also discuss the behavior as $t \to \infty$. At the simplest level we show that $(X, C) \to (1,1)$ and $(\hat{X}, \hat{C}) \to (1,1)$ as expected. We also discuss the asymptotic limit of (P′) as $\varepsilon \to 0$ and show the various ways in which the solution of (P′) tends to the solution of the pseudo-steady-state problem $(\hat{\mathrm{P}}')$. This relationship requires us to take into account the fact that since $C_0(x) \ne \hat{C}_0(x)$, the limit cannot hold for $t = 0$.

THEOREM 3.1. *Let $0 \le X_0(x) \le 1$, and let $0 \le C_0(x) \le 1$, with $C_0(x)$ satisfying* (3.2) *and* (3.3). *Then the solution $(X, C)$ of* (P′) *has the properties*

$$t \to (X(t,x), C(t,x)) \textit{is monotonically increasing for any } x \in \Omega$$

*and*

$$\lim_{t\to\infty} (X, C) = (1,1) \quad \textit{in } C([0,\infty) \times \bar{\Omega}).$$

*Proof.* It is easy to see that $(X_0(x), C_0(x))$ is a subsolution of (P′). We conclude from Theorems 2.1 and 2.2 that

$$X_0(x) \le X(t,x) \le 1, \qquad C_0(x) \le C(t,x) \le 1.$$

From these inequalities, we see at once that, for any $h > 0, (X(t+h,x), C(t+h,x))$ is a supersolution of (P′) so that $X(t+h,x) \geq X(t,x)$ and $C(t+h,x) \geq C(t,x)$. Hence $(X, C)$ increases monotonically in time. By the monotone convergence theorem there exists $(X_\infty(x), C_\infty(x))$ with $0 \leq X_\infty \leq 1, 0 \leq C_\infty \leq 1$ such that $\lim_{t\to\infty}(X, C) = (X_\infty, C_\infty)$ in $L^p(\Omega)$ for any $p$ with $1 \leq p \leq \infty$. On the other hand, using the definition of weak solutions and the monotonicity of $F$ and $g$, it is not difficult to show (see the argument in Sattinger [23]) that $(X_\infty, C_\infty)$ must be the solution of the stationary problem. □

COROLLARY 3.1. *If* $0 \leq X_0(x) \leq 1$ *and* $0 \leq C_0(x) \leq 1$, *then the solution of* (P′) *satisfies* $\lim_{t\to\infty}(X, C) = (1, 1)$.

*Proof.* Since $C_0$ does not necessarily satisfy (3.2) and (3.3), $C(t, \cdot)$ may not be monotone. Consider, however, the solution $(X^\#, C^\#)$ of (P′) with initial data $(X_0, 0)$. Then $(X^\#, C^\#)$ is easily seen to be a subsolution of (P′) with initial data $(X_0, C_0)$ so that

$$0 \leq X^\# \leq X \leq 1, \qquad 0 \leq C^\# \leq C \leq 1.$$

By Theorem 3.1, $(X^\#, C^\#)$ tends monotonically to $(1, 1)$ as $t \to \infty$, so that $(X, C)$ also tends to $(1, 1)$ as $t \to \infty$ (but perhaps not monotonically). □

For the pseudo-steady-state problem $(\hat{\mathrm{P}})$, the monotonicity in time of $\hat{X}$ and $\hat{C}$ is always guaranteed. The straightforward proof is omitted.

THEOREM 3.2. *If* $(\hat{X}, \hat{C})$ *is the solution of* $(\hat{\mathrm{P}}')$, *then*

$$t \to (\hat{X}(t,x), \hat{C}(t,x)) \textit{ is monotonically increasing}$$

*for any* $x \in \Omega$ *and* $\lim_{t\to\infty}(\hat{X}, \hat{C}) = (1, 1)$.

**3.2. Monotonicity in $\varepsilon$ and the relationship between (P) and $(\hat{\mathrm{P}})$.** Consider problem (P′) for fixed $\lambda$ and fixed initial data $(X_0, C_0)$, but with different values of $\varepsilon$. To emphasize the dependence on $\varepsilon$ we relabel the problem (P′) as $(P'_\varepsilon)$ and its solution as $(X^\varepsilon, C^\varepsilon)$. When is there monotonicity of $(\mathrm{P}'_\varepsilon)$ with respect to $\varepsilon$? In practice, $\varepsilon$ is often small and problem $(\hat{\mathrm{P}}')$ with initial value $\hat{X}_0 = X_0$ (and $\hat{C}_0$ determined from (3.4)) is used to approximate $(\mathrm{P}'_\varepsilon)$. In what sense, if any, is this a good approximation?

We begin with two simple lemmas.

LEMMA 3.1. *Let* $\varepsilon_1 \geq \varepsilon_2 \geq 0$; *let* $C_0(x)$ *satisfy* (3.2) *and* (3.3); *and let* $(X^i, C^i)$, $i = 1, 2$ *be the solutions of* $(\mathrm{P}'_\varepsilon)$ *corresponding to* $\varepsilon = \varepsilon_i$ *and initial data independent of* $i$. *Then*

$$(X^1, C^1) \leq (X^2, C^2) \quad \textit{for any } (t, x).$$

*Proof.* Since $X_t^1 \geq 0$ and, by Theorem 3.1, $C_t^1 \geq 0$, we have $\varepsilon_2 C_t^1 - \Delta C^1 + \lambda F(X^1) g(C^1) = (\varepsilon_2 - \varepsilon_1) C_t^1 \leq 0$, so that $(X^1, C^1)$ is a lower solution to $(\mathrm{P}'_\varepsilon)$ with $\varepsilon = \varepsilon_2$. Hence, for all $(t, x)$, we have

$$(X^1(t,x), C^1(t,x)) \leq (X^2(t,x), C^2(t,x)) \leq (1, 1). \qquad \square$$

*Remark* 3.1. If, for instance, (3.2) does not hold at some point $x$, then we can have $C^1(t,x) > C^2(t,x)$ for small $t$.

LEMMA 3.2. *If* $(X_0, C_0) \leq (\hat{X}_0, \hat{C}_0)$ *then* $(X(t,x), C(t,x)) \leq (\hat{X}(t,x)\hat{C}(t,x))$.

*Proof.* We have

$$\varepsilon \hat{C}_t - \Delta \hat{C} + \lambda F(\hat{X}) g(\hat{C}) = \varepsilon \hat{C}_t \geq 0,$$

where the last inequality follows from Theorem 3.2. In view of the assumption on the initial values, $(\hat{X}, \hat{C})$ is a supersolution of (P′) and the result follows. □



*Remark* 3.2. If $X_0 = \hat{X}_0$ and $C_0 = \hat{C}_0$, we conclude that problem $(\hat{\mathrm{P}}')$ converts solid more quickly than (P′), as expected.

These two lemmas lead to the following theorem, which deals with the limit as $\varepsilon \to 0$ of $(P'_\varepsilon)$.

THEOREM 3.3. *If* $(X_0, C_0) \leq (\hat{X}_0, \hat{C}_0)$, *then* $(X^\varepsilon, C^\varepsilon) \leq (\hat{X}, \hat{C})$ *and* $\lim_{\varepsilon\to 0}(X^\varepsilon, C^\varepsilon) = (\hat{X}, \hat{C})$ *in* $C((0,\infty) \times \Omega)$. *Moreover* $\varepsilon \to X^\varepsilon(t,x)$ *is monotone increasing for any* $t, x$, *and if* $C_0(x)$ *also satisfies* (3.2) *and* (3.3), $\varepsilon \to C^\varepsilon(t,x)$ *is monotone increasing as well.*

*Proof.* Suppose $C_0$ satisfies (3.2), (3.3); then, by Lemma 3.1, $(X^\varepsilon, C^\varepsilon)$ is monotone in $\varepsilon$ and so converges to $(\tilde{X}, \tilde{C})$ as $\varepsilon \to 0+$, uniformly on $\bar{\Omega}_T$; moreover, $(\tilde{X}, \tilde{C})$ clearly satisfies the pseudo-steady-state problem $(\hat{\mathrm{P}}')$ and therefore $\tilde{X} = \hat{X}, \tilde{C} = \hat{C}$. Now let $(X_\#^\varepsilon, C_\#^\varepsilon)$ be the unique solution of $(\mathrm{P}'_\varepsilon)$ with initial data $(X_0, 0)$; then $(X_\#^\varepsilon, C_\#^\varepsilon)$ is seen to be a subsolution to $(\mathrm{P}'_\varepsilon)$ for the same $\varepsilon$ and initial data $(X_0, C_0)$. It then follows from Lemma 3.2 that

$$(X_\#^\varepsilon, C_\#^\varepsilon) \leq (X^\varepsilon, C^\varepsilon) \leq (\hat{X}, \hat{C}).$$

But $(X_\#^\varepsilon, C_\#^\varepsilon)$ satisfies the conditions of Lemma 3.1, so it is monotone increasing in $\varepsilon$ and therefore tends to $(\hat{X}, \hat{C})$ as $\varepsilon \to 0+$. Hence, so does $(X^\varepsilon, C^\varepsilon)$. □

In the following theorem we provide other measures of how well $(\hat{\mathrm{P}}')$ approximates $(\mathrm{P}'_\varepsilon)$ for $\varepsilon$ small. The initial data for $(\mathrm{P}'_\varepsilon)$ is $(X_0, C_0)$, and for $(\hat{\mathrm{P}}')$ is $(\hat{X}_0 = X_0, \hat{C}_0)$, where $\hat{C}_0$ is determined from (3.4).

THEOREM 3.4. *Let* $X_0 \in C^\delta(\Omega)$ *for some* $\delta \in (0,1)$ *and let* $C_0 \in C^{2+\delta}(\Omega)$ *with* $(0,0) \leq (X_0, C_0) \leq (1,1)$. *Then the estimate* (2.6) *holds replacing* $(S^* = 1 - X^*, C^*)$ *by* $(\hat{S} = 1 - \hat{X}, \hat{C})$. *In particular,*

$$\|X^\varepsilon(t,x) - \hat{X}(t,x)\|_{L^1(\Omega)} \leq M\varepsilon \tag{3.5}$$

*for any* $t \geq 0$ *(i.e.,* $X^\varepsilon \to \hat{X}$ *in* $C([0,\infty) : L^1(\Omega))$ *as* $\varepsilon \to 0$), *where* $M = \frac{1}{\lambda}\|C_0 - \hat{C}_0\|_{L^1(\Omega)}$. *Moreover, if*

$$\|C_0 - \hat{C}_0\|_{L^1(\Omega)} \leq L\varepsilon^\gamma \quad \textit{for some } L > 0 \textit{ and } \gamma > 0, \tag{3.6}$$

*then*

$$\|X^\varepsilon(t,x) - \hat{X}(t,x)\|_{L^1(\Omega)} \leq \varepsilon^{\gamma+1}\frac{L}{\lambda} \tag{3.7}$$

*and*

$$\|C^\varepsilon(t,x) - \hat{C}(t,x)\|_{L^1(\Omega)} \leq L\varepsilon^\gamma \tag{3.8}$$

*for any* $t \geq 0$ *(i.e.,* $(X^\varepsilon, C^\varepsilon) \to (\hat{X}, \hat{C})$ *in* $C([0,\infty) : L^1(\Omega))$ *as* $\varepsilon \to 0$).

*Proof.* By Theorem 3.2 we have $\hat{C}_t \geq 0$ so that $\varepsilon \hat{C}_t - \Delta \hat{C} + \lambda F(\hat{X}) g(\hat{C}) \geq 0$ and the proof of Theorem 2.2 gives the inequality

$$\varepsilon \int_\Omega |C^\varepsilon(t,x) - \hat{C}(t,x)|\, dx + \lambda \int_\Omega |X^\varepsilon(t,x) - \hat{X}(t,x)|\, dx$$
$$+ \frac{1}{\alpha}\int_0^t \int_{\partial\Omega} |C^\varepsilon(\tau,\sigma) - \hat{C}(\tau,\sigma)|\, d\tau\, d\sigma \leq \varepsilon \int_\Omega |C_0(x) - \hat{C}_0(x)|\, dx,$$

which leads to the desired results (3.7) and (3.8). □

The next result shows the convergence of $(X^\varepsilon, C^\varepsilon)$ to $(\hat{X}, \hat{C})$ as $\varepsilon \to 0$ in the space $L^1(0, t : C(\bar{\Omega}))$ independently of the initial difference $\|C_0 - \hat{C}_0\|_{L^\infty(\Omega)}$.

THEOREM 3.5. *Let $X_0, C_0$ be as in Theorem 3.4 and let $C_0 \le \hat{C}_0$. Let $w \in C^\infty(\Omega)$ be the (unique) solution of the linear problem* (1.11). *Then, for any $t > 0$ and any $x \in \bar{\Omega}$,*

$$0 \le \int_0^t (\hat{C}(\tau, x) - C^\varepsilon(\tau, x))\, d\tau \le \varepsilon w(x) \tag{3.9}$$

*and*

$$0 \le \int_\Omega (\hat{X}(t, x) - X^\varepsilon(t, x))\, dx \le \varepsilon \frac{|\Omega|}{\lambda}, \tag{3.10}$$

*so that*

$$C^\varepsilon \to \hat{C} \quad in\ L^1(0, t : C(\bar{\Omega}))$$

*and*

$$X^\varepsilon \to \hat{X} \quad in\ L^\infty(0, t : L^1(\bar{\Omega})).$$

*Proof.* Integrate the equations for $C^\varepsilon$ and $\hat{C}$ with respect to time; use Lemma 3.2 and the comparison principle to obtain (3.9). Inequality (3.10) follows from Green's formula.

## 4. On the conversion of the solid and the penetration of the gas.[1]

**4.1. Solid conversion.** The behavior of $f(S)$ near $S = 0$ will determine whether or not the solid is fully converted in finite time.

THEOREM 4.1. *Consider problems* (P) *and* $(\hat{\mathrm{P}})$ *and let*

$$R(S) = \int_S^1 \frac{d\sigma}{f(\sigma)}, \qquad I = R(0+). \tag{4.1}$$

*Then if $I < \infty$, the solid is fully converted in finite time; if $I = \infty, S(x,t)$ and $\hat{S}(x,t)$ are positive for all $t$ at every $x$ where the initial solid concentration is positive.*

*Proof.* We carry out the proof for problem (P), the reasoning being similar for $(\hat{\mathrm{P}})$. We write (1.1) with its initial condition (1.4a) as

$$S_t = -\mu(t, x) f(S), \quad t > 0, \qquad S(0, x) = S_0(x), \tag{4.2}$$

and treat each $x$ individually. If $S_0(\xi) = 0$, then $S(t, \xi) \equiv 0$ for all $t$, so we confine ourselves to points $x$ where $S_0(x) > 0$. In that case, $S(t, x)$ will itself be positive for some initial time interval, and we can divide (4.2) by $f(S)$ to obtain

$$\frac{d}{dt} R(S) = \mu(t, x), \tag{4.3}$$

where $R(S)$ is defined by (4.1). Note that $R(S)$ is positive and decreasing on $0 < S < 1$. Therefore, $R^{-1}(S)$ is positive and decreasing on $[0, I)$. Integrating (4.3) from 0 to $t$ gives

$$R(S) = R(S_0) + \int_0^t \mu(\tau, x)\, d\tau,$$

[1] In this section $\|\cdot\|$ will stand for the usual sup norm on the $x$ variable, $\|u(t,x)\| = \sup_{x\in\Omega} \|u(t,x)\|$.



and therefore

$$S(t, x) = R^{-1}\left[\int_0^t \mu(\tau, x)\, d\tau + R(S_0(x))\right] \tag{4.4}$$

is the solution of (4.2) as long as $S > 0$. If $I = \infty$, the positivity of $R^{-1}$ on $[0, \infty)$ guarantees that $S(t, x) > 0$, so that the second part of the theorem is proved. If $I$ is finite, (4.4) furnishes a positive solution of (4.2) for $t < T(x)$ where $T(x)$ is defined by

$$R(S_0(x)) + \int_0^T \mu(\tau, x)\, d\tau = I.$$

At $t = T(x), S(x, t) = 0$ and remains equal to zero for $t \ge T(x)$. Since $R^{-1}(I) = 0$, it is useful to extend the definition of $R^{-1}$ through the rule $R^{-1}(z) = 0, z \ge I$. With that agreement (4.4) remains valid for all $t$ even if $I$ is finite.

Returning to (1.1) we can then write

$$\begin{aligned} S(t, x) &= R^{-1}\left[\int_0^t g(C(\tau, x))\, d\tau + R(S_0(x))\right] \\ &\le R^{-1}\left[\int_0^t g(C(\tau, x))\, d\tau\right]. \end{aligned} \tag{4.5}$$

We have proved in §3 that $C(t, x)$ tends to 1 as $t \to \infty$, uniformly for $x \in \bar{\Omega}$, so that $\int_0^t g(C(\tau, x))\, d\tau \ge I$ for all $x$ if $t$ is sufficiently large. Therefore, there exists $T$ such that $S(t, x) \equiv 0, t \ge T$, and we have *full conversion in finite time.* □

COROLLARY 4.1. *If $f(S) = S^m, I$ is finite if and only if $m < 1$. The explicit formulas are*

$$R_m(S) = \begin{cases} \frac{1 - S^{1-m}}{1-m}, & m \ne 1, \\ -\ln S, & m = 1, \end{cases}$$

*and thus*

$$R_m^{-1}(z) = \begin{cases} [1 - z(1-m)]_+^{1/1-m}, & m \ne 1, \\ e^{-z}, & m = 1, \end{cases} \tag{4.6}$$

*where $[u]_+$ stands for the greater of $u$ and 0. We can then rewrite* (4.5) *as*

$$S(t, x) = S_0(x) R_m^{-1}\left[S_0^{-1}(x) \int_0^t g(C(\tau, x))\, d\tau\right].$$

*Remark* 4.1. We could substitute (4.5) into (1.2) to obtain a nonlinear integro-differential equation for $C$ subject to conditions (1.4b) and (1.4c). A related approach due to McNabb [19] is more useful. He introduces

$$\eta(t, x) = \int_0^t [1 - C(\tau, x)]\, d\tau \qquad (1 - C = \eta_t), \tag{4.7}$$

the time-integrated deviation of $C$ from its steady state. A straightforward calculation shows that $\eta$ satisfies

$$\begin{aligned} &\varepsilon\eta_t - \Delta\eta = \varepsilon(1 - C_0) + \lambda(S_0 - S), \quad x \in \Omega, \quad t > 0; \\ &\eta(x, 0) = 0, \quad \eta + \alpha\eta_\nu = 0, \quad x \in \partial\Omega, \quad t > 0. \end{aligned} \tag{4.8}$$

Although $S$ is unknown in (4.8), considerable information can nevertheless be extracted from this formulation. For instance, because $S$ decreases to 0 as $t \to \infty, \eta(t, \cdot)$ is monotonically increasing to the solution $\eta_\infty(x)$ of the steady-state problem

$$-\Delta \eta_\infty = \varepsilon(1 - C_0) + \lambda S_0, \quad \eta_\infty + \alpha \eta_{\infty,\nu} = 0, \quad x \in \partial\Omega. \tag{4.9}$$

Note that

$$\eta_\infty \leq (\varepsilon + \lambda) w(x), \tag{4.10}$$

where $w(x)$ is the solution of (1.11).

For the p.s.s. problem we define

$$\hat{\eta} = \int_0^t (1 - \hat{C})\, d\tau, \tag{4.11}$$

which satisfies

$$-\Delta \hat{\eta} = \lambda(\hat{S}_0 - \hat{S}), \quad \hat{\eta} + \alpha \hat{\eta}_\nu = 0, \quad x \in \partial\Omega, \tag{4.12}$$

and $\hat{\eta}(t, x)$ tends monotonically to the solution of

$$-\Delta \hat{\eta}_\infty = \lambda \hat{S}_0, \quad \hat{\eta}_\infty + \alpha \hat{\eta}_{\infty,\nu} = 0, \quad x \in \partial\Omega. \tag{4.13}$$

We see that

$$\hat{\eta}_\infty \leq \lambda w(x). \tag{4.14}$$

In the *special case where* $g(C) = C$, (4.5) gives

$$S(t, x) = R^{-1}[t - \eta + R(S_0)],$$

which can be substituted into (4.8) to give a scalar partial differential equation for $\eta$. These ideas were exploited in [24] and [28] and will be used to some extent in the remainder of the section.

*Remark* 4.2. If we had considered a problem *without gas diffusion* and with a gas concentration *maintained at the value one,* the solid concentration $S^*(t, x)$ would satisfy the ordinary differential equation

$$S_t^* = -f(S^*), \quad t > 0, \quad S^*(0, x) = S_0^*(x). \tag{4.15}$$

There are many ways of seeing that $S^*(t, x) \leq S(t, x)$, where $S$ is the solution of (P) with the same initial solid concentration (and any $C_0 \leq 1$). For instance, since $R^{-1}$ is monotone decreasing and $g(C) \leq 1$, (4.5) shows that

$$S(t, x) \geq R^{-1}(t + R(S_0(x))),$$

the right-hand side being precisely $S^*(t, x)$, because now $\mu \equiv 1$ in (4.4). Similarly, we can show $S^* \leq \hat{S}$, the solution of $(\hat{\mathrm{P}})$ with the same initial value.

The quantity that is perhaps of greatest physical interest is the overall conversion fraction $\gamma(t)$. The inverse of this function gives the time required to achieve the



conversion of a specified fraction of the solid. We shall compare problems (P), (P′), and (4.15) with the same initial value $S_0(x)$.

The *overall conversion* at time $t$ for problem (P) is given by

$$\gamma(t) = \frac{\int_\Omega (S_0(x) - S(t, x))\, dx}{\int_\Omega S_0(x)\, dx} = 1 - \frac{\int_\Omega S(t, x)\, dx}{\int_\Omega S_0(x)\, dx}, \tag{4.16}$$

for problem $(\hat{\mathrm{P}})$ by

$$\hat{\gamma}(t) = 1 - \frac{\int_\Omega \hat{S}(t, x)\, dx}{\int_\Omega S_0(x)\, dx},$$

and for (4.15) by

$$\gamma^*(t) = 1 - \frac{\int_\Omega S^*(t, x)\, dx}{\int_\Omega S_0(x)\, dx}.$$

We have already proved the following properties:

(a) $0 \leq \gamma(t) \leq 1, \quad 0 \leq \hat{\gamma}(t) \leq 1, \quad 0 \leq \gamma^*(t) \leq 1;$

(b) $\gamma(t) \leq \hat{\gamma}(t), \quad \hat{\gamma}(t) = \gamma^*(t)$ (see Remark 4.2);

(c) *If* $C_0(x) \leq \hat{C}_0(x), \quad \gamma(t) \leq \hat{\gamma}(t)$ (see Lemma 3.2);

(d) $\lim_{t\to\infty} \gamma(t) = \lim_{t\to\infty} \hat{\gamma}(t) = \lim_{t\to\infty} \gamma^*(t) = 1$ (see Corollary 3.1).

If $I$ is finite, Theorem 4.1 tells us that the solid is fully converted in finite time, that is, $\gamma(t) \equiv 1$ for $t$ sufficiently large. We define full conversion times $t_1, \hat{t}_1, t_1^*$ by

$$t_1 = \inf\{t : \gamma(t) = 1\}, \quad \hat{t}_1 = \inf\{t : \hat{\gamma}(t) = 1\}, \quad t_1^* = \inf\{t : \gamma^*(t) = 1\}.$$

We first observe that $t_1^*$ is known explicitly. We seek the smallest value of $t$ for which $S^*(t, x)$, the solution of (4.15), is identically zero on $\bar{\Omega}$. Since $\|S_0\| = 1$, there is at least one point $\xi$ where $S_0(\xi) = 1$. These points will be the slowest to convert. From (4.4) we have $S(t, \xi) = R^{-1}(t)$, which is positive for $t < I$ and vanishes for $t \geq I$. Therefore, $t_1^* = I$.

From (b) and (c) above we see that

$$t_1 \geq I, \quad \hat{t}_1 \geq I \quad \text{and, if} \quad C_0(x) \leq \hat{C}_0(x), \quad t_1 \geq \hat{t}_1.$$

We can obviously characterize $t_1$ by

$$\inf\{t : S(t, x) \equiv 0, x \in \bar{\Omega}\} = \inf\{t : X(t, x) \equiv 1, x \in \bar{\Omega}\}.$$

By (4.5) and the fact that $R^{-1}(I) = 0$, we also have that $t_1$ is characterized by

$$\min_{x \in \bar{\Omega}} \int_0^{t_1} g(C(\tau, x))\, d\tau + R(S_0(x)) = I$$

and $\hat{t}_1$ by

$$\min_{x \in \bar{\Omega}} \int_0^{\hat{t}_1} g(\hat{C})\, d\tau + R(\hat{S}_0) = I.$$

If $S_0(x) = \hat{S}_0(x) \equiv 1$, then we see that $t_1$ and $\hat{t}_1$ satisfy

$$\min_{x \in \bar{\Omega}} \int_0^{t_1} g(C)\, d\tau = I, \qquad \min_{x \in \bar{\Omega}} \int_0^{\hat{t}_1} g(\hat{C})\, d\tau = I. \tag{4.17}$$

Next, we provide estimates for $\hat{t}_1$ when $\hat{S}_0(x) \equiv 1$, the case that occurs most frequently in applications (uniform initial solid concentration).

THEOREM 4.2. *Let $\hat{S}_0 \equiv 1$ and let $I$ be finite. Assume there exist $g_1, g_2 \in C^0([0,1]) \cap C^1((0,1))$ such that $g_1', g_2' \geq 0, g_1(1) = g_2(1) = 1$, and*

$$g_1(r) \leq g(r) \leq g_2(r) \quad \forall\, r \in [0,1]. \tag{4.18}$$

*Then*

$$I + M_2\lambda\|w\| \leq \hat{t}_1 \leq I + M_1\lambda\|w\|, \tag{4.19}$$

*where $M_1 = \sup_{[0,1]} g_1'$, $M_2 = \inf_{[0,1]} g_2'$, and $w$ is defined by (3.9).*

*Proof.* By definition, $\hat{\eta}_t = 1 - \hat{C}$ so that $0 \leq 1 - \hat{\eta}_t \leq 1, 0 \leq \hat{\eta}_t \leq 1$. We immediately see that with $M_1, M_2$ as defined above,

$$1 - g_1(1-\hat{\eta}_t) \leq M_1\hat{\eta}_t, \qquad 1 - g_2(1-\hat{\eta}_t) \geq M_2\hat{\eta}_t,$$

and, therefore,

$$1 - M_1\hat{\eta}_t \leq g_1(1-\hat{\eta}_t) \leq g(1-\hat{\eta}_t) \leq g_2(1-\hat{\eta}_t) \leq 1 - M_2\hat{\eta}_t.$$

Integrating from 0 to $\hat{t}_1$, we find

$$t_1 - M_1\hat{\eta}(\hat{t}_1, x) \leq \int_0^{\hat{t}_1} g(1-\hat{\eta}_t)\, d\tau \leq \hat{t}_1 - M_2\hat{\eta}(\hat{t}_1, x),$$

and, taking the minimum with respect to $x$ and using the characterization (4.17) for $\hat{t}_1$, we obtain

$$\hat{t}_1 - M_1\|\hat{\eta}(\hat{t}_1, x)\| \leq I \leq \hat{t}_1 - M_2\|\hat{\eta}(\hat{t}_1, x)\|. \tag{4.20}$$

When $t \geq \hat{t}_1, \hat{S} = 0$ so that (4.12) gives

$$\hat{\eta} = \hat{\eta}_\infty = \lambda w(x), \qquad \|\hat{\eta}(t_1, x)\| = \lambda\|w\|,$$

which, when substituted into (4.20) gives the result (4.19). $\square$

*Remark* 4.3. Special cases of interest correspond to $g(C) = C^p, p > 0$. Our estimates then become

(4.21) (a) if $p = 1$, $\quad \hat{t}_1 = I + \lambda\|w\| \quad$ (take $g_1 = g_2 = g$);

(b) if $p < 1$,

(4.22) $I + p\lambda\|w\| \leq \hat{t}_1 \leq I + \lambda\|w\| \quad$ (take $g_1(r) = r, g_2 = g$);

(c) if $p > 1$,

(4.23) $I + \lambda\|w\| \leq \hat{t}_1 \leq I + \lambda p\|w\| \quad$ (take $g_2(r) = r, g_1 = g$).

The result (a) was first given in [28]. From the inequality $0 \leq \int_0^{\hat{t}_1}(1-\hat{\eta}_t)\, d\tau = \hat{t}_1 - \lambda w(x)$, we also find

$$\hat{t}_1 \geq \lambda\|w\|, \tag{4.24}$$



which improves the lower bound (b) if $\lambda(1-p)\|w\| \geq I$.

Further improvement follows from using Jensen's inequality, which we illustrate in the case $p < 1$, when the inequality becomes

$$\left(\int_0^t v(\tau)\, d\tau\right)^p \geq t^{p-1}\int_0^t v^p(\tau)\, d\tau,$$

where $v(t)$ is any nonnegative continuous function.

Setting $v = 1 - \hat{\eta}_t$, we find

$$\int_0^{\hat{t}_1}(1-\hat{\eta}_t)^p\, d\tau \leq \hat{t}_1^{1-p}(\hat{t}_1 - \lambda w(x))^p \quad \forall x \in \bar{\Omega},$$

and, taking the minimum over $x$,

$$I \leq \hat{t}_1^{1-p}(\hat{t}_1 - \lambda\|w\|)^p.$$

This inequality implies $\hat{t}_1 \geq T$, where $T$ is the unique positive solution of

$$I = T^{1-p}(T - \lambda\|w\|)^p, \tag{4.25}$$

which can be shown to always provide a better lower bound to $\hat{t}_1$ than (4.22) and (4.24). As an example, if $p = \frac{1}{2}$, (4.25) gives

$$T = \frac{\lambda\|w\| + \sqrt{\lambda^2\|w\|^2 + I^2}}{2},$$

which is larger than the lower bounds (4.22) and (4.24).

We now turn to estimates for $t_1$ when $S_0(x) \equiv 1$. These are somewhat more difficult as $t_1$ also depends on both $\varepsilon$ and $C_0(x)$. We will not be able, for instance, to find an exact value for $t_1$ when $p = 1$, as we did for $\hat{t}_1$ (see (4.21)).

THEOREM 4.3. *Let $S_0(x) \equiv 1, 0 \leq C_0(x) \leq 1$; then*

$$t_1 \leq I + M_1(\varepsilon + \lambda)\|w\|,$$

*and if also $C_0 \leq \hat{C}_0$, then*

$$t_1 \geq \hat{t}_1 \geq I + M_2\lambda\|w\|,$$

*where $M_1, M_2$ are as in Theorem 4.2.*

*Proof.* We proceed as in Theorem 4.2 to reach the equivalent of (4.20):

$$t_1 - M_1\|\eta(t_1, x)\| \leq I \leq t_1 - M_2\|\eta(t_1, x)\|. \tag{4.26}$$

Unfortunately, $\eta(t_1, x)$ is not known explicitly, so we must use estimates for $\|\eta(t_1, x)\|$. From (4.9) we have

$$\eta(t, x) \leq \eta_\infty(x) \leq (\varepsilon + \lambda)w(x),$$

which yields

$$t_1 \leq I + M_1(\varepsilon + \lambda)\|w\|,$$

the upper bound in Theorem 4.3. The lower bound in the theorem follows from previous results (Theorem 4.2 and Lemma 3.2). $\square$

*Remark* 4.4. Again we can consider the case $C^p$ and find corresponding forms of (4.21)–(4.24). For instance, (4.21) becomes

$$I + \lambda\|w\| \le t_1 \le I + (\lambda+\varepsilon)\|w\|,$$

which is quite satisfactory as long as $\varepsilon$ is small.

*Remark* 4.5. Jensen's inequality can be used to improve some of the bounds.

*Remark* 4.6. We can also be more accurate in our estimate for $\|\eta(t_1,x)\|$, which appears in the proof of Theorem 4.3. For $t \ge t_1, \eta(t,x)$ satisfies (4.8) with $S_0 \equiv 1, S \equiv 0$; that is,

$$-\Delta\eta = \varepsilon(1-C_0) + \lambda - \varepsilon\eta_t; \quad \eta + \alpha\eta_\nu = 0 \quad \text{on } \partial\Omega.$$

Now $0 \le \eta_t \le 1$, so that

$$\lambda - \varepsilon C_0 \le -\Delta\eta \le \varepsilon(1-C_0) + \lambda$$

and, hence,

$$\lambda w(x) - \varepsilon y(x) \le \eta(t,x)) \le (\lambda+\varepsilon)w(x) - \varepsilon y(x),$$

where $y(x)$ satisfies

$$-\Delta y = C_0(x), \quad x \in \Omega; \quad y + \alpha y_\nu = 0 \quad \text{on } \partial\Omega.$$

As an illustration of the use of these inequalities, suppose $C_0 \equiv 1$. Then (4.26) yields

$$t_1 - M_1\lambda\|w\| \le I \le t_1 - M_2(\lambda-\varepsilon)\|w\|$$

and

$$I + M_2(\lambda-\varepsilon)\|w\| \le t_1 \le I + \lambda M_1\|w\|.$$

If, also, $p = 1$, then with $g_1 = g_2 = g$, we find $M_1 = M_2 = 1$ and

$$I + (\lambda-\varepsilon)\|w\| \le t_1 \le I + \lambda\|w\| = \hat{t}_1.$$

Thus, unlike the case where $C_0 \le \hat{C}_0$, we now have $t_1 \le \hat{t}_1$.

**4.2. Penetration of the gas.** In problems (P) and ($\hat{\text{P}}$), the gas concentration tends uniformly to its steady state $C = \hat{C} = 1$. The concentration must therefore be strictly positive for $t$ sufficiently large, but is this necessarily true for all $t > 0$? Our experience with scalar problems involving strong absorption suggests otherwise: there may exist a time-dependent "dead core" in which the concentration is zero at time $t$ (see [4] and [9]). Any such dead core must, of course, disappear in finite time. For problems (P) and ($\hat{\text{P}}$) we define

$$D(t) = \{x \in \Omega : C(t,x) = 0\}, \qquad T = \inf\{t : C(t,x) > 0 \text{ for all } x \in \bar{\Omega}\}, \tag{4.27}$$

$$\hat{D}(t) = \{x \in \Omega : \hat{C}(t,x) = 0\}, \qquad \hat{T} = \inf\{t : \hat{C}(t,x) > 0 \text{ for all } x \in \bar{\Omega}\}. \tag{4.28}$$

As in the scalar case, an important role is played by

$$J = \int_{0+}^{1} \frac{d\sigma}{\sqrt{G(\sigma)}}, \quad \text{where } G(\sigma) = \int_0^\sigma g(C)\,dC. \tag{4.29}$$



Note that if $g(C) = C^p$, $J$ is finite for $0 < p < 1$ and infinite if $p \ge 1$.

Our main result is that (a) no dead core exists if $J = \infty$, and (b) a dead core may exist if $J$ is finite. We prove these assertions below and also provide rough estimates for the location of the dead core and for the time at which it disappears.

THEOREM 4.4. *Let $g(C)$ be such that $J = \infty$. Then*

$$\hat{C}(t,x) > 0 \quad \textit{for all } (t,x) \in [0,\infty) \times \bar{\Omega},$$
$$C(t,x) > 0 \quad \textit{for all } (t,x) \in (0,\infty) \times \bar{\Omega}.$$

*Proof.* By Theorem 3.2, $\hat{C}(t,x)$ increases monotonically in time, so $\hat{C}(t,x) \ge \hat{C}_0(x)$ with $\hat{C}_0$ defined by (1.9). Thus $\hat{C}_0(x)$ satisfies

$$-\Delta\hat{C}_0 + \lambda g(\hat{C}_0) \ge 0$$

and, therefore, by a result of Vázquez [30], $\hat{C}_0(x) > 0$ in $\bar{\Omega}$, and hence $\hat{C}(t,x) > 0$ in $\bar{\Omega}$ for all $t \ge 0$. In the parabolic case, we have

$$0 = \varepsilon C_t - \Delta C + \lambda f(S)g(C) \le \varepsilon C_t - \Delta C + \lambda g(C),$$

so that $C(t,x)$ is a supersolution of the scalar problem

$$\varepsilon C_t^* - \Delta C^* + \lambda g(C^*) = 0 \quad \text{on } (0,\infty)\times\Omega,$$
$$C^* + \alpha C_\nu^* = 1 \quad \text{on } (0,\infty)\times\partial\Omega,$$
$$C^*(0,x) = C_0(x) \quad \text{on } \Omega.$$

The strict positivity can be obtained by an easy modification of a result of Bertsch, Kersner, and Peletier [5] and, therefore, $C(t,x) > 0$ on $(0,\infty)\times\bar{\Omega}$. □

Next we show that if $J$ is finite, a dead core is possible in the pseudo-steady-state case.

THEOREM 4.5. *Let $J < \infty$; define*

$d(x,\partial\Omega) =$ *distance from $x$ to $\partial\Omega$,*
$A =$ *half-width of thinnest slab enclosing $\Omega$,*
$r_i =$ *radius of largest inscribed ball,*
$$m(t) = f(\inf_{x\in\bar{\Omega}} \hat{S}(t,x)), \qquad M(t) = f(\sup_{x\in\bar{\Omega}} \hat{S}(t,x)).$$

*Then*

$$\hat{D}(t) \supset \left\{x \in \Omega : d(x,\partial\Omega) \ge \left[\frac{N}{2\lambda m(t)}\right]^{1/2} J\right\}, \tag{4.30}$$

$$\hat{D}(t) \ne \emptyset \quad \textit{when} \quad \left[\frac{N}{2\lambda m(t)}\right]^{1/2} J < r_i, \tag{4.31}$$

$$\hat{D}(t) = \emptyset \quad \textit{when } \lambda < \frac{J^2}{2a^2M(t)}. \tag{4.32}$$

$$\hat{D}(t) = \emptyset \quad \textit{for all } t \textit{ if } \lambda < J^2/2a^2. \tag{4.33}$$

*Proof.* Since $f$ is increasing, we have

$$-\Delta\hat{C} + \lambda M(t)g(\hat{C}) \ge 0 = -\Delta\hat{C} + \lambda f(\hat{S})g(\hat{C}) \ge -\Delta\hat{C} + \lambda m(t)g(\hat{C}),$$

so that $\hat{C}$ is a subsolution of the scalar elliptic problem

$$-\Delta C^{(\alpha)} + \lambda m(t) g(C^{(\alpha)}) = 0, \qquad x \in \Omega,$$
$$C^{(\alpha)} + \alpha C^{(\alpha)}_\nu = 1, \qquad x \in \partial\Omega.$$

Therefore, $\hat{C}(t,x) \le C^{(\alpha)}(t,x)$, which, in turn, is smaller than the solution $C^{(0)}(t,x)$ of the Dirichlet problem. It follows that $\hat{D}(t)$ is contained in the dead core of $C^{(0)}(t,x)$. It is shown in Diaz [7, Prop. 1.11] that the dead core for $C^{(0)}$ satisfies (4.30); see also [8] and [25]. The assertion (4.31) is an immediate consequence of (4.30).

To prove (4.32) we observe that $\hat{C}$ is a supersolution to the scalar problem with $M(t)$ replacing $f(\hat{S})$. Although conditions for nonexistence of a dead core for this latter problem are available [17], [26], we confine ourselves to the case $\alpha = 0$, when the simple bound (4.32) is derived in [3]. Since $M(t)$ is a decreasing function of time with $M(0) = 1$, the bound (4.33) follows. □

*Remark* 4.7. To apply (4.31), we need an explicit lower bound for $m(t)$. Such a bound is easily obtained if $\inf_{\bar{\Omega}} \hat{S}_0(x) = \delta > 0$. Then, from Remark 4.2, we find $\hat{S}(t,x) \ge R^{-1}(t + R(\delta))$ so that $m(t) \ge f[R^{-1}(t+R(\delta))]$ and $m(0) \ge f(\delta)$. Therefore, a dead core exists at time $t$ if

$$r_i > J\left\{\frac{N}{2\lambda f[R^{-1}(t+R(\delta))]}\right\}^{1/2}. \tag{4.34}$$

In particular, a dead core exists for sufficiently small $t$ if

$$r_i > J\left\{\frac{N}{2\lambda f(\sigma)}\right\}^{1/2}. \tag{4.35}$$

Note that (4.34) also gives a lower bound for $\hat{T}$:

$$\hat{T} \ge R\left\{f^{-1}\left(\frac{J^2 N}{2\lambda r_i^2}\right) - R(\delta)\right\}. \tag{4.36}$$

We now turn to the parabolic problem when $J < \infty$. Estimates are more cumbersome because the dead core may not be monotonic in $t$. For instance, if $C_0(x) = 1$, a dead core may form after a certain time and later disappear. We can, however, find an upper bound on $T$, the time beyond which $C(t,x) > 0$ for all $x \in \bar{\Omega}$. We confine ourselves to the Dirichlet problem ($\alpha = 0$).

THEOREM 4.6. *Let $\alpha = 0, J < \infty$, and let $a$ be the half-width of the thinnest strip enclosing $\Omega$. Then*

$$T \le \frac{\varepsilon + \lambda}{2} a^2, \qquad \hat{T} \le \frac{\lambda}{2} a^2. \tag{4.37}$$

Our proof is based on comparison with a half-space, so we begin with the following lemma.

LEMMA 4.1. *Consider problem* (P′) *for the half-space $x > 0$ with $C(t,0) = 1$ for $t > 0$ and initial values $0 \le X(0,x) \le 1, 0 \le C(0,x) \le 1$. Let*

$$\rho(t) = \inf\{x : C(t,x) \equiv 0\}$$



*be the penetration distance of the gas, where $\rho(t)$ is understood to be $+\infty$ if $C(x,t) > 0$ for all $x$. Then*

$$\rho^2 \ge \frac{2t}{\varepsilon + \lambda}, \tag{4.38}$$

*an estimate which holds even when $\varepsilon = 0$.*

*Proof of Lemma* 4.1. We give the proof for $\varepsilon > 0$, omitting the simpler case $\varepsilon = 0$. Let us first consider the problem with *zero initial values* for $C$ and $X$. Condition (3.2) being satisfied, $C(t,\cdot)$ and $\rho(t)$ are monotonically increasing. We write (2.3) as

$$\varepsilon C_t - C_{xx} = -\lambda X_t, \quad x > 0, \quad t > 0$$

and, as in [14], integrate in time from 0 to $t$ to obtain

$$\varepsilon C(t,x) + \lambda X(t,x) = \psi_{xx}, \tag{4.39}$$

where

$$\psi(t,x) = \int_0^t C(\tau,x)\,d\tau.$$

We multiply (4.39) by $x$ and integrate from $x = 0$ to $x = \rho(t)$:

$$\int_0^\rho x(\varepsilon C + \lambda X)\,dx = \int_0^\rho x\psi_{xx}\,dx = t - \psi(t,\rho(t)).$$

By the time monotonicity, $C(\tau,\rho(t)) = 0$ for $\tau < t$, so that $\psi(t,\rho(t)) = 0$. Thus we find

$$t = \int_0^\rho x[\varepsilon C + \lambda X]\,dx \le (\varepsilon + \lambda)\frac{\rho^2}{2},$$

which proves (4.38) for zero initial values. For other initial values the gas concentration $C(t,x)$ will be larger (Property I, §3.1), and (4.38) must remain true. □

*Proof of Theorem* 4.6. Let $(X_\Omega, C_\Omega)$ be the solution of the problem (P′) with $\alpha = 0$. We compare this solution with the solution $(X_H, C_H)$ for a supporting half-space $H$ enclosing $\Omega$ with initial values $(X_H(0,x), C_H(0,x)) \le (X_\Omega(0,x), C_\Omega(0,x))$. Then, since $C_H \le 1$ on $\partial\Omega, (X_H(t,x), C_H(t,x))$ is a subsolution to (P′) for $\Omega$, and hence

$$C_\Omega(t,x) \ge C_H(t,x). \tag{4.40}$$

Now let $U$ be the thinnest slab enclosing $\Omega$; applying (4.40) successively to the half-spaces corresponding to the two faces of $U$, we see that $C_\Omega(t,x) > 0$ when $t > \frac{\varepsilon+\lambda}{2}a^2$, where $a$ is the half-width of the slab. This yields (4.37). The proof is the same for the pseudo-steady-state case. □

*Remark* 4.8. When full conversion occurs in finite time ($I < \infty$), we have estimated $t_1$ and $\hat{t}_1$, the times to full conversion. When $t > t_1$ (or $t > \hat{t}_1$ in the p.s.s. case), the equation for the gas concentration is just the ordinary heat equation, which has the well-known property $C > 0$ for the given boundary conditions. Hence $t_1$ is an upper bound for $T$.

We end this section by showing that a dead core can occur for the half-space problem when $g(C) = C^p, p < 1$. Consider again the Dirichlet problem, now with

$C(0,x) = S(0,x) = 1$, the initial condition on $C$ being least favorable for generating a dead core. Our problem then becomes

$$\begin{aligned} &\varepsilon C_t - C_{xx} = -\lambda f(S) g(C) = \lambda S_t, \quad x > 0, \quad t > 0; \\ &C(0,x) = S(0,x) = 1, \qquad C(t,0) = 1. \end{aligned} \tag{4.41}$$

Since conversion of the solid is fastest at $x = 0$, we have

$$f(S(t,0)) \leq f(S(t,x)) \leq 1.$$

From the second inequality we find that $C(t,x) \geq z(t)$, where $z(t)$ is the solution of $z_t = -\lambda g(z), z(0) = 1$. Because $z > 0$ for

$$t < K \doteq \int_0^1 \frac{dz}{g(z)},$$

we see that, as expected, $C(t,x)$ is strictly positive for $t < K$. Note that when $g(z) = z^p, K$ is finite if and only if $p < 1$. Next we show that $C$ develops a dead core at later times by constructing a supersolution $D(t,x)$ of (4.41) over a bounded time interval with $D(t,x) = 0$ for $x$ sufficiently large and some range of $t$. Since $S(t,0)$ satisfies $S_t = -f(S)$ with initial value one, we find that $S(t,0) = R^{-1}(t)$ (see (4.5) and (4.6)). Because $S(t,0)$ decreases monotonically from 1 to 0, we can find, for each $\delta$ with $0 < \delta < 1$, a time $T_\delta$ such that

$$f(S(t,0)) \geq 1 - \delta, \qquad 0 < t < T_\delta.$$

Therefore, $f(S(t,x)) \geq 1 - \delta$ for $0 < t < T_\delta$ and $C(t,x) \leq D(t,x)$ on $(0, T_\delta)$ where $D$ satisfies the scalar problem

$$\begin{cases} \varepsilon D_t - D_{xx} = -\lambda(1-\delta) g(D), & x > 0, \quad t > 0; \\ D(0,x) = 1, \qquad D(t,0) = 1. \end{cases} \tag{4.42}$$

It was shown in [32] that problem (4.42) exhibits a dead core for all $t > \frac{\varepsilon K}{\lambda(1-\delta)}$. Therefore, (4.41) will have a dead core if we can choose the parameters so that

$$\frac{\varepsilon K}{\lambda(1-\delta)} < T_\delta. \tag{4.43}$$

Let us illustrate the calculation for the case $f(S) = S$. Then $S(t,0) = e^{-t}, T_\delta = -\log(1-\delta)$, and (4.43) is satisfied if, for some $\delta, 0 < \delta < 1$, we have

$$\frac{\varepsilon K}{\lambda} < -(1-\delta)\log(1-\delta).$$

The maximum of the right side occurs at $\delta = 1 - \frac{1}{e}$, and the maximal value is 1. Thus (4.41) will have a dead core if $\frac{\varepsilon K}{\lambda} < 1$.

*Remark* 4.9. A *bounded* domain $\Omega$ of sufficiently large size will also have a dead core for a suitable choice of the parameters. Of course, in this case the dead core must disappear in finite time.



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