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## A MATHEMATICAL MODEL FOR OUTGASSING AND CONTAMINATION\*

W. FANG†, M. SHILLOR†, E. STAHEL†, E. EPSTEIN‡, C. LY‡,  
J. MCNIEL‡, AND E. ZARON‡

**Abstract.** A model for the mathematical description of the processes of outgassing and contamination in a vacuum system is proposed. The underlying assumptions are diffusion in the source, convection and diffusion in the cavity, mass transfer across the source-cavity interface, and a generalization of the Langmuir isotherm for the sorption kinetics on the target. Three approximations are considered where the asymptotic behavior of the model for large time is shown as well as the dependence and sensitivity of the model on some of the parameters. Some numerical examples of the full model are then presented together with a proof of the uniqueness of the solution.

**Key words.** outgassing, contamination, convection-diffusion, generalized Langmuir conditions, sorption kinetics

**AMS(MOS) subject classifications.** 35K, 67R

**1. Introduction.** We consider a mathematical model for the description of processes of outgassing and adsorption of contaminants. Such processes are very common and are of considerable importance in the vacuum technology and in the aerospace industry. The motivation for this study comes from the latter, where these processes have received increasing attention in recent years.

Contamination refers to a number of processes whereby molecules or particles of a material settle or adsorb on a clean surface, called the "target," forming undesirable layers, which may impair the functions of the surface. In satellites such surfaces are optical instruments, or thermal control panels (see, e.g., Scialdone [27] and references therein). In vacuum applications the surfaces affected are various instruments in the vacuum chamber (see, e.g., Dayton [12] or Roth [26]). In the electronics industry these are various parts of microelectronic circuits and other elements (see Benson et al. [2] and references therein), and in the food packaging industry these surfaces are the foodstuff that becomes contaminated. Therefore, there is a considerable interest, from the applied point of view, in controlling outgassing-related contamination. Indeed, uncontrolled contamination in satellites may reduce their efficiency, render some of the sensitive equipment inoperative, and even shorten the lifetime of the satellite itself (see, e.g., Scialdone [28] or Glassford and Liu [16], and references therein).

The processes related to contamination are physisorption, chemisorption, nucleation, bulk condensation, desorption, evaporation, and surface diffusion (see, e.g., Sigsbee [30], Fujita [13], Hayward and Trapnell [20], and Glassford and Liu [16]). These processes are fields of active research; nevertheless, they are not well understood at the present time.

Outgassing refers to the migration of molecules of a chemical from a material into its surroundings. Generally these processes are governed by diffusion in the bulk material and desorption from its surface (see, e.g., [16]).

A source of outgassing is molecules trapped or produced during the manufacturing process in the bulk material or acquired afterwards as a result of exposure to the environment. Another source is the molecules produced continuously as a result of

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chemical reactions within the bulk material or by exposure to ultraviolet radiation in outer space.

There exists a vast literature on various physical and chemical aspects of outgassing and contamination; those references include Aris [1], Carter [7], Crank and Park [10], Gortel et al. [17], Hayward and Trapnell [20], Missel and Glang [23], Roth [26], Sigsbee [30], etc.

Recently, Glassford and Liu [15] performed an extensive literature search related to space applications. They provide a detailed bibliography of almost 900 publications, reports, and books. Moreover, in [16], they give a thorough survey of the analytical models and experimental methods relevant to outgassing and contamination. In [14], Glassford and Garrett propose the standardization of the relevant measurement methods.

Glassford and Liu emphasize in [15] and [16] the need for a coherent picture for the processes, based upon physical and chemical principles, as opposed to the common practice in the industry, where each specific situation is considered on its own.

We adopt this approach and propose a mathematical model which gives a unified description of outgassing and contamination. It is a step on the way to a comprehensive model, capable of sufficiently accurate predictions in applications. Therefore, the setting is simplified, it includes only the essential elements, appropriately interconnected.

The geometry of the model consists of four regions, or compartments (see Fig. 2.1 below), the source, the source-cavity interface, the cavity, and the target. The source might be a layer of paint, a plastic part, an epoxy layer, etc. The cavity represents outer space or the inside of the vacuum chamber in some applications. The target is a clean surface where we are interested in the monitoring of adsorption of the contaminant. It is easy to modify the model for other geometrical settings with multiple sources and targets.

The assumptions that underlie our model are as follows. The contaminant consists of only one species, an assumption that can be generalized but would unnecessarily complicate the presentation and the notation. The method of migration is by diffusion in the source. The rate of migration to the source-cavity interface is proportional to the deviation from equilibrium of the concentrations in the material and on the surface. A similar assumption applies to the rate of desorption from the surface into the cavity. In addition, we allow the degradation of the surface itself, resulting in surface production of contaminants. The migration of the contaminant in the cavity is controlled by diffusion and convection. In applications where the pressures are atmospheric (as in the electronics industry), diffusion is the primary transport mechanism. This is not the case in outer space or in a vacuum chamber where diffusion is limited and cannot be the main means of transport. There, the main transport mechanism is a convective current. It was considered in the literature (see [15] and [16], and references therein), but none of the approaches seems to be satisfactory. Formally, we may be tempted to solve the Boltzmann equation (see, e.g., [8]) for this current, but, since we need to specify the boundary conditions that are unknown—their form is proposed below—such an approach is not yet feasible. It seems that, in the present, some knowledge about the convective current may be obtained by considering an appropriate inverse problem. That is, we may use our model in conjunction with experimental results to obtain information about the convective current. Such problems are usually termed “coefficient identification” problems. In the model we propose diffusion and convection in the cavity. But in the cases of high vacuum the diffusion may be considered as a small perturbation or a regularization of the system of equations. It preserves the overall structure of the model. Finally, on the target, we consider a generalization of the

Langmuir isotherm sorption (see, e.g., [26], [12], [16]), where we take into account the change in the characteristics of the sorption process, when the target surface becomes completely covered, by the contaminant, and henceforth the adsorbing molecules no longer encounter the clean surface, but only other molecules of their kind.

We would like to stress that the novelty of our model is in putting all four elements together in one setting. The main effort, at this stage, should be concentrated on the validation of the conditions on the source-cavity interface and on the target, and the mathematical ways to express these conditions. The treatment of the mass transfer mechanism in the cavity should be considered at later stages.

There are other known processes that can influence outgassing and contamination considerably, which we do not include. Among them we mention the existence of electric fields and their influence on the motion of charged contaminant molecules (as in satellites, see [27], [18], and [19]) and the existence of temperature and pressure gradients (see [16] and [15], and references therein). It is possible to take these into account at later stages.

Some of the coefficients that enter the model can be found in the literature, e.g., the diffusion coefficients, some of the rate functions, and the equilibrium partition coefficients, while others still need to be measured, such as some of the rate functions. Also, some additional research is certainly necessary in establishing the form of the source function. Finally, the sensitivity of the model to the various parameters needs a detailed investigation.

This model, once validated, should augment the standard method of materials testing used in the aerospace industry, adopted by NASA (the so-called ASTM E595 test), where a sample material is left for 24 hours in a vacuum chamber, to decide whether it meets the required standard. The drawbacks of this test are that it cannot detect materials that over the years degrade in space and outgas over long periods of time causing considerable contamination, nor can it detect materials that outgas considerably over short periods of time but then remain "clean" afterward.

The model, presented in § 2, consists of four partial differential equations for the volume concentrations of the contaminant in the source and in the cavity, and for its surface concentration on the source-cavity interface and on the target (see Fig. 2.1) together with the relevant initial and boundary conditions.

To study various parts of the model, three approximations are presented in § 3. First, we consider a problem for the averaged concentrations, the "well-mixed" model. It consists of four ordinary differential equations and is somewhat similar to the model in Zeiner [32], although not so cumbersome. It allows us to study, in particular, the rate of decay to the steady state. Second, we study the source to cavity migration across the interface by considering the source and the cavity to be semi-infinite. Under suitable assumptions we obtain a closed-form solution and investigate its dependence on the parameters. Finally, we consider the complete model in one-space dimension by reducing it to a set of Volterra integral equations, which are solved numerically to obtain the fluxes and the concentrations on the source-cavity interface and on the target surface.

In order to study the model numerically, an iterative scheme for the time-discretized model is considered in § 4. A computer program was written with this scheme as its basis. The behavior of the solution is shown graphically in some examples.

Finally, in § 5 we prove, using the energy method, that the model admits at most one solution; that is, the solution if existing is unique. The existence of a solution is proved in Busenberg, Fang, and Shillor [4] using the theory of semigroups for a more general model.

The system considered in this paper is semilinear with nonlinear boundary conditions, as well as diffusion on the boundaries. It is nonstandard and the uniqueness result for such systems is not obvious. It is mathematically of some interest in addition to its direct relevance to the wellposedness of our model.

**2. The model.** In this section we construct the mathematical model. Our aim is a relatively simple model for the description of the main features of the processes of outgassing and contamination. For this reason we assume that the system is isothermal and electrically neutral. Nevertheless, for completeness we indicate below how these assumptions can be relaxed.

Let us consider only one species of contaminant and denote its concentration by  $C = C(x, y, z, t)$  (mole/cm<sup>3</sup>). We take the geometric setting shown in Fig. 2.1.

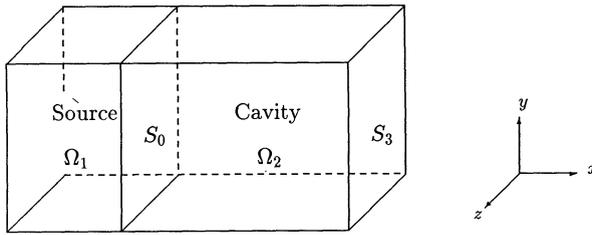


FIG. 2.1. The geometric setting.

The *source* of contamination  $\Omega_1$  is a region of solid material (e.g., metal, plastic, or a coat of paint, etc.) that initially has a certain concentration of contaminant trapped in it (assumed to be a known function of position, usually taken as a constant) due to its manufacturing process or atmospheric exposure. We include the possibility that the parent material itself can degrade under the influence of chemical reactions or ultraviolet radiation and produce volatile contaminant molecules. Let  $f_1$  be the rate of contaminant production (mole/cm<sup>3</sup> sec) in  $\Omega_1$ , possibly dependent on space, time, and concentration. Assuming that these molecules move randomly inside the host material or matrix, the evolution of the concentration  $C_1$  of contaminant is controlled by the diffusion equation in  $\Omega_1$ , that is,

$$\frac{\partial C_1}{\partial t} = \nabla \cdot (D_1 \nabla C_1) + f_1,$$

where  $D_1$  (cm<sup>2</sup>/sec) is the diffusion coefficient, a function of position and concentration, and  $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$  is the gradient operator.

Consider the *cavity*  $\Omega_2$ . This can represent a vacuum chamber or outer space. If we consider the processes as taking place at ordinary temperature and pressure, we can assume that diffusion is the means of migration of the contaminant. Since we are motivated in part by aerospace and vacuum applications, we postulate, in addition, the existence of a convection term that represents the collisionless migration of the molecules from the source to the target when the pressure and temperature are low. The assumption about diffusion in space or vacuum applications serves only as a regularization of the system. Nevertheless, although the density of molecules in space is very low, there are many collisions among them, since they are ionized. Therefore, some diffusionlike behavior is found, as can be seen in [18] and [19]. Otherwise, we would have considerable difficulty in explaining the accumulation of contaminants on windows that face the empty space. Thus it is assumed that there exists a velocity field  $\vec{v} = \vec{v}(x, y, z, t)$  in  $\Omega_2$  that transports the contaminant in space. The evolution of the

contaminant concentration  $C_2$  in  $\Omega_2$  is therefore described by the convection-diffusion equation

$$\frac{\partial C_2}{\partial t} = \nabla \cdot (D_2 \nabla C_2) - \vec{v} \cdot \nabla C_2,$$

where  $D_2$  is the diffusion coefficient for the cavity, a function of space and concentration.

*Remark.* As was noted in the Introduction, we may attempt solving the Boltzmann equation to obtain the transport in the cavity. But in order to solve the Boltzmann equation we need boundary conditions (see, e.g., [8]) and these are the main concern of our model. This is so even in the case where the Knudsen number is large [8, p. 232], as in space applications. Thus, solving for the convection current seems to be impractical. Therefore, one possibility is to consider it as an experimental input. A more interesting way is to determine it as follows. Given the model we may construct an inverse problem for the determination of  $\vec{v}$ , such that, for a certain class of possible  $\vec{v}$ 's we seek the one that best fits the given experimental results. The "best fit" has to be made precise. There is considerable interest recently in inverse problems in identifying various coefficients in models, once some information about the solutions is obtained.

Now we turn to consider the *source-cavity interface*  $S_0$ . This is the surface from which the contaminant emerges into the cavity. There is a considerable amount of published work (see, e.g., [15], [16], and references therein) concerning the various processes that take place on such a surface, the so-called "surface condensation kinetics," which are relevant to outgassing and contamination. These are the adsorption, desorption, and physisorption processes as well as nucleation, bulk condensation, evaporation, surface diffusion, etc. Despite the amount of research done it seems that the understanding of these processes is fairly limited. Therefore we consider a simple approach to the description of the surface processes. More complicated or sophisticated forms could be used, but would complicate the model without any apparent benefit at this stage. Such modifications, however, might be needed in later stages.

Let  $\theta_0$  be the surface concentration of contaminant molecules (mole/cm<sup>2</sup>) on  $S_0$ . Then the rate of change of  $\theta_0$  is given by the rate of surface production  $f_0$  (mole/cm<sup>2</sup> sec) and the difference between the incoming flux from the source  $-D_1(\partial C_1/\partial n)$ , and the outgoing flux into the cavity  $-D_2(\partial C_2/\partial n) + v_n C_2$ . The function  $f_0$  represents creation on the surface of contaminant molecules by material degradation caused by (impinging) radiation or by chemical reactions and may depend on position and concentration. There is some indication (Dayton [11], [16] and Rheed [24], and references therein) that surface diffusion may be important for some types of surfaces; though we neglect surface diffusion here, it is considered in [4]. Thus on  $S_0$

$$\frac{\partial \theta_0}{\partial t} = -D_1 \frac{\partial C_1}{\partial n} - \left( -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 \right) + f_0,$$

where the normal  $\vec{n}$  is out of  $\Omega_1$  (into  $\Omega_2$ ) and  $v_n = \vec{v} \cdot \vec{n}$  is the normal component of  $\vec{v}$  on  $S_0$ . This just represents mass conservation. The physics enters via our assumption that the fluxes are proportional to deviations from equilibrium between  $\theta_0$  and  $C_1$ ,  $\theta_0$ , and  $C_2$ , respectively, that is,

$$\begin{aligned} -D_1 \frac{\partial C_1}{\partial n} &= h_1(C_1 - \gamma_1 \theta_0), \\ -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 &= h_2(\gamma_2 \theta_0 - C_2). \end{aligned}$$

Here  $\gamma_1$  and  $\gamma_2$  are the so-called "equilibrium partition coefficients," taken as constants, so that in equilibrium  $C_1 = \gamma_1\theta_0$  and  $C_2 = \gamma_2\theta_0$ . The rate coefficients  $h_1$  and  $h_2$ , also called the "effective flow resistance coefficients" (see, e.g., [16]), are given functions of position and concentrations. We can generalize this condition and replace  $h_1(C_1 - \gamma_1\theta_0)$  by a function  $H_1$  that depends on  $\theta_0$  and on  $C_1 - \gamma_1\theta_0$ , i.e.,  $H_1 = H_1(\theta_0, C_1 - \gamma_1\theta_0)$ . It is assumed to be a given function of two arguments, say  $r$  and  $s$ . The case  $s = 0$  represents the equilibrium state where  $C_1 = \gamma_1\theta_0$  and the flux is required to vanish in this case, that is,  $H_1(r, 0) = 0$  (for  $r \geq 0$ ). The flux should be positive (adsorption) if  $s > 0$  (i.e.,  $C_1 > \gamma_1\theta_0$ ) and be negative (desorption) if  $s < 0$  (i.e.,  $C_1 < \gamma_1\theta_0$ ), thus  $H(r, s)s > 0$  for  $s \neq 0$ ,  $r \geq 0$ . Similarly, we can replace  $h_2(\gamma_2\theta_0 - C_2)$  by  $H_2(\theta_0, \gamma_2\theta_0 - C_2)$ , with properties similar to those of  $H_2$ .

The initial concentration of contaminant  $\theta_0^0$  on the surface  $S_0$  is assumed to be known.

Next we consider the *target surface*  $S_3$  where contamination takes place. This may be a lens or a thermal control surface, or a quartz microbalance. All that was said above concerning  $S_0$  applies to  $S_3$  with the simplification that the flux is from one side only and there is no surface source. Thus if  $\theta$  is the surface concentration (mole/cm<sup>2</sup>) on  $S_3$ , then its evolution is governed by

$$\frac{\partial \theta}{\partial t} = -D_2 \frac{\partial C_2}{\partial n} + v_n C_2,$$

where  $\vec{n}$  is the outward normal to  $\Omega_2$  on  $S_3$ , surface diffusion being neglected.

The flux on  $S_3$  is assumed to satisfy

$$-D_2 \frac{\partial C_2}{\partial n} + v_n C_2 = H(\theta, C_2).$$

We proceed to describe the *sorption* function  $H$ . Since we take it to be a generalization of a standard way to consider contamination on a partially covered surface, we first give a short description of the latter.

Let  $\eta$  be the surface covering, that is the fraction of the surface (locally) that is covered by adsorbing molecules. Then the rate of growth of  $\eta$  is given by (see, e.g., [12], [16], or [30])

$$(2.1) \quad n_s \frac{d\eta}{dt} = n_i s (1 - \eta) - \frac{n_2}{\tau} \eta,$$

where  $n_i$  is the impinging flux per unit area of the surface (molecules/cm<sup>2</sup> sec),  $s$  is the sticking coefficient,  $n_s$  is the number of adsorption sites per unit area, and  $\tau$  is the adsorption residence time. It is assumed that there is no dissociation of the molecules upon adsorption, otherwise  $(1 - \eta)$  should be replaced by  $(1 - \eta)^j$  where  $j$  is the degree of dissociation.

In equilibrium there holds

$$(2.2) \quad n_i = N_A p / (2\pi MRT)^{1/2},$$

where  $p$  is the pressure,  $T$  the temperature,  $R$  the gas constant,  $N_A$  Avogadro's number, and  $M$  the molecular weight. Also, typically,

$$\tau = \tau_0 \exp(E_a/RT),$$

where  $E_a$  is desorption energy and  $\tau_0$  the vibrational period of the molecules in the adsorbed state. When the system is in a steady state ( $d\eta/dt = 0$  in (2.1)) we obtain the

Langmuir isotherm (see, e.g., [16], [15], and references therein)

$$(2.3) \quad \eta = \frac{n_s \sigma \tau}{n_s + n_s \sigma \tau}.$$

A quantum-mechanical description of desorption with low coverage can be found in Gortel et al. [17] and in Kreuzer and Teshima [22].

Now we consider the sorption function  $H$ . In (2.1) the first term depends (via the pressure) on the concentration in the cavity and the second term depends only on the covering  $\eta$ . Analogously, we assume that

$$(2.4) \quad H(\theta, C_2) = -K_1(\theta) + K_2(\theta)C_2.$$

The first term on the right-hand side represents *desorption* and the second one represents *adsorption*. Since we are interested in the case where a multilayer covering exists, in addition to the single-layer case, we use the surface concentration  $\theta$  instead of the surface covering  $\eta$ . If  $\theta_{\max}$  is the concentration needed to have a monolayer covering of the entire surface, then  $\eta = \theta/\theta_{\max}$  for  $\theta \leq \theta_{\max}$  (i.e., partial covering). Also, once we have more than one layer, the adsorption and desorption are from the top layer and are likely to be independent of the surface material (although they do depend on the surface morphology) and independent of the concentration  $\theta$ . A simple way to take this into account is to postulate that

$$(2.5) \quad K_1(\theta) = k_1(\theta_{\max} - (\theta_{\max} - \theta)_+),$$

where  $k_1$  is a constant and

$$(\theta_{\max} - \theta)_+ = \begin{cases} \theta_{\max} - \theta & \text{if } \theta_{\max} - \theta > 0, \\ 0 & \text{if } \theta_{\max} - \theta \leq 0. \end{cases}$$

The graph of the function  $K_1(\theta)$  is depicted in Fig. 2.2. It is seen that for  $\theta < \theta_{\max}$  (i.e., partial covering by a single layer),  $K_1(\theta)$  is linear in  $\theta$ , while for  $\theta \geq \theta_{\max}$  it is independent of  $\theta$ .

A similar argument leads to

$$(2.6) \quad K_2(\theta) = K(k_2\theta_{\max} + (\theta_{\max} - \theta)_+),$$

where  $K$  and  $k_2$  are constants. The graph of  $K_2$  is depicted in Fig. 2.2.

In equilibrium the sorption function satisfies  $H(\theta, C_2) = 0$ , hence

$$\begin{aligned} -k_1\theta_{\max} + Kk_2C_2\theta_{\max} &= 0 && \text{if } \theta \geq \theta_{\max}, \\ -k_1\theta + KC_2(k_2\theta_{\max} + (\theta_{\max} - \theta)) &= 0 && \text{if } \theta < \theta_{\max}, \end{aligned}$$

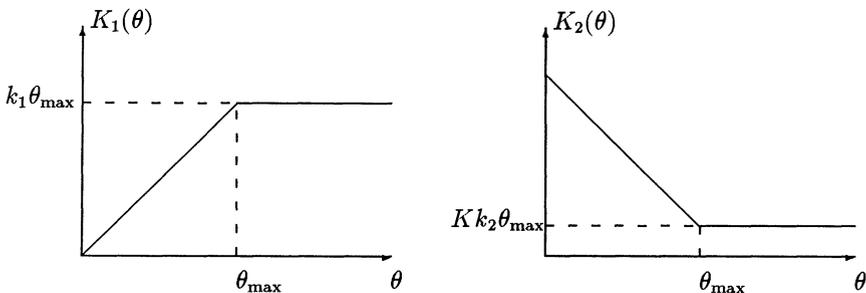


FIG. 2.2. The graphs of  $K_1(\theta)$  and  $K_2(\theta)$ .

and therefore

$$C_2 = \frac{k_1}{Kk_2} \quad \text{if } \theta \geq \theta_{\max},$$

$$\theta = \frac{KC_2(1+k_2)\theta_{\max}}{k_1 + KC_2} \quad \text{if } \theta < \theta_{\max}.$$

In equilibrium, for  $\theta \geq \theta_{\max}$ , it follows that if we use the ideal gas law  $C_2 = P/(RT)$ , where  $P$  is the vapor pressure and  $T$  the temperature, we obtain

$$\frac{k_1}{Kk_2} = \frac{P}{RT}.$$

Moreover, if  $\theta < \theta_{\max}$ , let  $\eta = \theta/\theta_{\max}$  be the surface covering, then

(2.7) 
$$\eta = \frac{KC_2(1+k_2)}{k_1 + KC_2}.$$

If  $k_2 \ll 1$  we recover the Langmuir isotherm (2.3). It seems that our approach is more general. Nevertheless, we may identify our coefficients with those of (2.3) as follows:

$$k_1 = n_s, \quad KC_2 = n_i s \tau.$$

In equilibrium  $C_2 = P/(RT)$  and  $n_i = N_A P / (2\pi MRT)^{1/2}$  (see (2.2)), hence

$$K \frac{P}{RT} = \frac{N_A P}{(2\pi MRT)^{1/2}} s \tau$$

or

$$Kk_2 = s \tau \left( \frac{RT}{2\pi M / N_A^2} \right)^{1/2}.$$

(See also [12, p. 105].) This clarifies the physical significance of  $k_1$ ,  $k_2$ , and  $K$ .

Other forms for the adsorption function are possible and ultimately it should be derived from statistical mechanics considerations. A similar construction for the outgassing process on  $S_0$  could be considered.

Note that all of the coefficients depend on temperature, pressure, and concentrations, and it is customary to take them in the (Arrhenius) form

$$k = k_* \exp(E/RT),$$

where  $k_*$  is the preexponential and  $E$  is the relevant energy (per mole) associated with the process.

In order to complete the description of the model we have to specify the rest of the boundary conditions. Let  $S_1 = \partial\Omega_1 \setminus S_0$  be the boundary of  $\Omega_1$  excluding  $S_0$ . Then for the sake of simplicity, we assume that there is no flux of contaminant through  $S_1$ , thus,  $\partial C_1 / \partial n = 0$  (this holds at all points of  $S_1$  where  $\vec{n}$  is defined).

Let  $S_2 = \partial\Omega_2 \setminus (S_0 \cup S_3)$  be the boundary of  $\Omega_2$  excluding  $S_0$  and  $S_3$ . In the case of satellites,  $\Omega_2$  represents outer space and it is natural to assume  $C_2 = 0$  on  $S_2$ ; that is, a molecule that crosses  $S_2$  is lost from the system. In vacuum technology we can take  $C_2 = 0$  if the outer wall of the vacuum chamber is very cold and whatever hits it sticks, or  $-D_2(\partial C_2 / \partial n) + v_n C_2 = 0$  if all the molecules are reflected back. We take an intermediate approach and assume a partial reflection governed by

$$-D_2 \frac{\partial C_2}{\partial n} + v_n C_2 = h_0 C_2,$$

where  $h_0$  is the rate coefficient. When  $h_0 \rightarrow \infty$  we recover the condition  $C_2 = 0$  on  $S_2$  while for  $h_0 \rightarrow 0$  we recover  $-D_2(\partial C_2/\partial n) + v_n C_2 = 0$ .

For simplicity, we assume below that the diffusion coefficients  $D_1$  and  $D_2$  and the partition coefficients are constants (we consider an isothermal system with constant pressure).

To summarize our model we have a system of four partial differential equations for the unknowns  $C_1, C_2, \theta_0,$  and  $\theta$ , together with the relevant boundary conditions. We now put it in a nondimensional form. Suppose that  $\tilde{C}_1, \tilde{C}_2, \tilde{\theta}_0,$  and  $\tilde{\theta}$  are the dimensional variables and let the nondimensional variables be  $C_1 = \tilde{C}_1/\max C_1^0, C_2 = \tilde{C}_2/\max C_1^0, \theta_0 = \tilde{\theta}_0/(a \max C_1^0),$  and  $\theta = \tilde{\theta}/(a \max C_1^0)$ . Here  $C_1^0$  is the initial concentration in the source. Take  $\tilde{\Omega}_1 = \{-a < \tilde{x} < 0, 0 < \tilde{y} < \tilde{b}, 0 < \tilde{z} < \tilde{b}\}$  and  $\tilde{\Omega}_2 = \{0 < \tilde{x} < \tilde{l}, 0 < \tilde{y} < \tilde{b}, 0 < \tilde{z} < \tilde{b}\}$  to be the source and cavity, respectively, and similarly  $\tilde{S}_0, \tilde{S}_1,$  etc. We set  $x = \tilde{x}/a, y = \tilde{y}/a, z = \tilde{z}/a$  and let  $l = \tilde{l}/a, b = \tilde{b}/a$  and denote by  $\Omega_1, \Omega_2, S_0, S_1,$  etc., the domains in  $(x, y, z)$ . Next we set  $t = \tilde{t}D_2/a^2$  as the time variable. With this notation our model is as follows.

We are seeking the functions  $(C_1, C_2, \theta_0, \theta)$  such that

$$(2.8) \quad \frac{\partial C_1}{\partial t} = d\Delta C_1 + f_1 \quad \text{in } \Omega_1, \quad t > 0,$$

$$(2.9) \quad C_1 = C_1^0 \quad \text{in } \Omega_1, \quad t = 0,$$

$$(2.10) \quad \frac{\partial C_1}{\partial n} = 0 \quad \text{on } S_1, \quad t > 0,$$

$$(2.11) \quad \frac{\partial C_2}{\partial t} = \Delta C_2 - \vec{v} \cdot \nabla C_2 \quad \text{in } \Omega_2, \quad t > 0,$$

$$(2.12) \quad C_2 = 0 \quad \text{in } \Omega_2, \quad t = 0,$$

$$(2.13) \quad -\frac{\partial C_2}{\partial n} + v_n C_2 = h_0 C_2 \quad \text{on } S_2, \quad t > 0,$$

$$(2.14) \quad \frac{\partial \theta_0}{\partial t} = -d \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} - v_x C_2 + f_0 \quad \text{on } S_0, \quad t > 0,$$

$$(2.15) \quad -d \frac{\partial C_1}{\partial x} = h_1 (C_1 - \gamma_1 \theta_0) \quad \text{on } S_0, \quad t > 0,$$

$$(2.16) \quad -\frac{\partial C_2}{\partial x} + v_x C_2 = h_2 (\gamma_2 \theta_0 - C_2) \quad \text{on } S_0, \quad t > 0,$$

$$(2.17) \quad \theta_0 = \theta_0^0 \quad \text{on } S_0, \quad t = 0,$$

$$(2.18) \quad \frac{\partial \theta}{\partial t} = -\frac{\partial C_2}{\partial x} + v_x C_2 \quad \text{on } S_3, \quad t > 0,$$

$$(2.19) \quad -\frac{\partial C_2}{\partial x} + v_x C_2 = H(C_2, \theta) \quad \text{on } S_3, \quad t > 0,$$

$$(2.20) \quad \theta = 0 \quad \text{on } S_3, \quad t = 0,$$

where we have used the notation

$$\begin{aligned} d &= D_1/D_2, & \gamma_1 &= a\tilde{\gamma}_1, & \gamma_2 &= a\tilde{\gamma}_2, \\ h_0 &= a\tilde{h}_0/D_2, & h_1 &= a\tilde{h}_1/D_2, & h_2 &= a\tilde{h}_2/D_2, \\ f_1 &= a^2\tilde{f}_1/(D_2 \max C_1^0), & f_0 &= a\tilde{f}_0/(D_2 \max C_1^0), & \vec{v} &= a\tilde{v}/D_2, \\ H(r, s) &= a\tilde{H}(r \max C_1^0, sa \max C_1^0)/D_2. \end{aligned}$$

Also  $S_0 = \{x = 0, 0 < y < b, 0 < z < b\}$  and hence  $\partial/\partial n = \partial/\partial x$  (out of  $\Omega_1$  and into  $\Omega_2$ ) and  $S_3 = \{x = l, 0 < y < b, 0 < z < b\}$  and so  $\partial/\partial n = \partial/\partial x$  (out of  $\Omega_2$ ).

The model is characterized by ten coefficients, two geometric constants  $b$  and  $l$ , and five "data functions"  $C_1^0$ ,  $\theta_0^0$ ,  $v$ ,  $f_0$ , and  $f_1$ , assumed to be known.

If we have more than one species of contaminant, a modified model would consist of a set of equations (2.8)–(2.20) for each species with some coupling among the equations.

There is some experimental evidence (see, e.g., [15], [16], and references therein, or [12, p. 102]) that in many cases of outgassing, contaminants originate from polymers, and outgassing is a diffusion controlled process; initially, the contaminants are present in the bulk of the source material in a nominally uniform distribution. Given these conditions our model simplifies; the initial condition is  $C_1^0 = \text{const.}$  in (2.9) and  $f_1 = 0$  in (2.8) since there is no production of the contaminant in the source. Moreover, since the process is diffusion controlled,  $h_1 \rightarrow \infty$  and we replace (2.15) by  $C_1 = \gamma_1 \theta_0$ . In space or vacuum systems, at least for short periods of time, if  $\theta_0 \approx 0$  we can take  $C_1 = 0$  on  $S_0$ . In such a case the problem decouples. We can solve for  $C_1$  in  $\Omega_1$  first (for all times  $t \geq 0$ ) and then solve the rest of the model using this known  $C_1$ .

We neglect the contributions to diffusion due to electric fields, pressure gradients, and temperature gradients, as it seems to be a reasonable assumption in many applications (see, e.g., Scialdone [29] concerning electric potentials on satellites and Glassford and Liu [16] concerning temperature or pressure gradients in space). On the other hand, the experiments of Hall, Stewart, and Hayes [18] and Hall and Wakimoto [19] suggest that in other applications electric potential may be important. Therefore we give a short description of how we can take into account electric fields (for ionized systems), pressure gradients, and temperature variations (see, e.g., Bird, Stewart, and Lightfoot [3]). Denote by  $\phi = \phi(x, y, z, t)$  the electric potential,  $T = T(x, y, z, t)$  the temperature, and  $p = p(x, y, z, t)$  the pressure (all in nondimensional form). We may write the diffusion in  $\Omega(\Omega_1$  or  $\Omega_2)$  as

$$(2.21) \quad \frac{\partial C}{\partial t} = -\nabla \cdot \vec{j} + f,$$

where  $\vec{j}$  is the contaminant flux and  $f$  is the volume source ( $f = 0$  in  $\Omega_2$ ). Above we used Fick's law  $\vec{j} = -D\nabla C$ .

In presence of an electric potential, temperature field, and pressure gradients, the total flux is [3, p. 567]

$$(2.22) \quad \vec{j} = \vec{j}_d + \vec{j}_p + \vec{j}_T + \vec{j}_\phi,$$

where the diffusion flux is  $\vec{j}_d = -D\nabla C$ , the pressure induced flux is  $\vec{j}_p = -D_p \nabla p$ , the temperature induced flux is  $\vec{j}_T = -D_T \nabla \log T$  and the electrically induced flux is  $\vec{j}_\phi = -D_\phi \nabla \phi$ , with  $D_p$ ,  $D_T$ , and  $D_\phi$  the corresponding coefficients.  $D_T$  is related to the Soret effect and  $D_p$  and  $D_\phi$  depend generally on temperature and concentration. Then the modified diffusion equation is (2.21) with the flux given by (2.22). Moreover, it is now necessary to solve the appropriate equations for the evolution of temperature, pressure, and electric potential together with the relevant boundary conditions. It is clear that this complicates the model considerably and as a first step we should study the model (2.8)–(2.20) neglecting these phenomena.

**3. Approximate models.** In order to gain some insight into the behavior of the model, we consider three one-dimensional (in space) approximations. Using these approximations enables us to simplify the investigation of various aspects of the model and relate them to the underlying physical processes.

For the sake of simplicity, throughout this section we neglect the convective term in the cavity, simplify the process on the target, and take all the coefficients as positive constants. Then the simplified model in one space dimension consists of the following system of partial differential equations with the relevant initial and boundary conditions:

Find the functions  $C_1(x, t)$ ,  $C_2(x, t)$ ,  $\theta_0(t)$ ,  $\theta(t)$ , such that

$$(3.1) \quad \frac{\partial C_1}{\partial t} = d \frac{\partial^2 C_1}{\partial x^2} + f_1, \quad -1 < x < 0, \quad t > 0,$$

$$(3.2) \quad C_1 = C_1^0, \quad -1 < x < 0, \quad t = 0,$$

$$(3.3) \quad \frac{\partial C_1}{\partial x} = 0, \quad x = -1, \quad t > 0,$$

$$(3.4) \quad \frac{\partial C_2}{\partial t} = \frac{\partial^2 C_2}{\partial x^2}, \quad 0 < x < b, \quad t > 0,$$

$$(3.5) \quad C_2 = 0, \quad 0 < x < b, \quad t = 0,$$

$$(3.6) \quad \frac{d\theta_0}{dt} = -d \frac{\partial C_1}{\partial x} + \frac{\partial C_2}{\partial x} + f_0, \quad x = 0, \quad t > 0,$$

$$(3.7) \quad -d \frac{\partial C_1}{\partial x} = h_1(C_1 - \gamma_1 \theta_0), \quad x = 0, \quad t > 0,$$

$$(3.8) \quad -\frac{\partial C_2}{\partial x} = h_2(\gamma_2 \theta_0 - C_2), \quad x = 0, \quad t > 0,$$

$$(3.9) \quad \theta_0 = \theta_0^0, \quad x = 0, \quad t = 0,$$

$$(3.10) \quad \frac{d\theta}{dt} = -\frac{\partial C_2}{\partial x}, \quad x = b, \quad t > 0,$$

$$(3.11) \quad -\frac{\partial C_2}{\partial x} = h_3(C_2 - \gamma_3 \theta), \quad x = b, \quad t > 0,$$

$$(3.12) \quad \theta = 0, \quad x = b, \quad t = 0,$$

where the notation is the same as in (2.8)–(2.20).

First, we consider the “well-mixed” approximation, and then an approximation of the outgassing process on the interface  $S_0$ . Finally, we reduce system (3.1)–(3.12) to a system of Volterra integral equations, which we solve numerically.

**3.1. The well-mixed approximation.** In this approximation we use the model (3.1)–(3.12) and examine the evolution in time of the total amount of the material (or numbers of particles) in  $\Omega_1$  and  $\Omega_2$ . Let

$$\bar{C}_1(t) = \int_{-1}^0 C_1(x, t) \, dx,$$

$$\bar{C}_2(t) = \int_0^b C_2(x, t) \, dx.$$

Then by integrating (3.1) and (3.4) with respect to  $x$  and using the boundary conditions (3.3), (3.7), (3.8), (3.11), together with (3.6) and (3.10), we obtain

$$(3.13) \quad \frac{d\bar{C}_1(t)}{dt} = -h_1(C_1(0, t) - \gamma_1\theta_0(t)) + \bar{f}_1(t),$$

$$(3.14) \quad \frac{d\theta_0}{dt} = h_1C_1(0, t) - (h_1\gamma_1 + h_2\gamma_2)\theta_0 + h_2C_2(0, t) + f_0(t),$$

$$(3.15) \quad \frac{d\bar{C}_2(t)}{dt} = -h_2C_2(0, t) - h_3C_2(b, t) + h_2\gamma_2\theta_0(t) + h_3\gamma_3\theta(t),$$

$$(3.16) \quad \frac{d\theta}{dt} = h_3(C_2(b, t) - \gamma_3\theta(t)),$$

where  $\bar{f}_1(t) = \int_{-1}^0 f_1(x, t) dx$  is the average of  $f_1$ .

In the “well-mixed” model, it is assumed that the concentrations are independent of the position  $x$ , that is

$$\begin{aligned} C_1(x, t) &\approx \bar{C}_1(t), & -1 \leq x \leq 0, \\ C_2(x, t) &\approx \bar{C}_2(t)/b, & 0 \leq x \leq b. \end{aligned}$$

*Remark.* Such an assumption underlies most of the models in the literature (see, e.g., [12], [11], [15], [16], [20], etc.) as it leads to a system of ordinary differential equations for the total masses.

By substituting these approximations into (3.13)–(3.16) and assuming that there are no contaminant production sources (i.e.,  $\bar{f}_1(t) = 0$  and  $f_0(t) = 0$ ), we obtain a system of ordinary differential equations for  $\bar{C}_1(t)$ ,  $\bar{C}_2(t)$ ,  $\theta_0(t)$ , and  $\theta(t)$ , which can be written in the following matrix form:

$$(3.17) \quad \frac{dU(t)}{dt} + AU(t) = 0,$$

where

$$U(t) = (\bar{C}_1(t), \theta_0(t), \bar{C}_2(t), \theta(t))^T$$

and

$$A = \begin{pmatrix} h_1 & -h_1\gamma_1 & 0 & 0 \\ -h_1 & h_1\gamma_1 + h_2\gamma_2 & -h_2/b & 0 \\ 0 & -h_2\gamma_2 & (h_2 + h_3)/b & -h_3\gamma_3 \\ 0 & 0 & -h_3/b & h_3\gamma_3 \end{pmatrix}.$$

The initial condition for (3.17) is

$$(3.18) \quad U(0) = (\bar{C}_1^0, \theta_0^0, 0, 0)^T.$$

The solution to (3.17) is characterized by the eigenvalues of matrix  $A$ . It is easy to verify that  $P^{-1}AP$  is symmetric and semipositive definite, where

$$P = \text{diag}(\sqrt{\gamma_1}, 1, \sqrt{\gamma_2 b}, \sqrt{\gamma_2/\gamma_3}).$$

Therefore the eigenvalues of  $A$ , which are the same as those of  $P^{-1}AP$ , are all real and satisfy

$$0 = \lambda_1 < \lambda_2 \leq \lambda_3 \leq \lambda_4.$$

The fact that  $A$  has a zero eigenvalue is related to the existence of a nontrivial steady state. Let  $X_1, X_2, X_3,$  and  $X_4$  be the corresponding linearly independent eigenvectors of  $A$ . It follows from the standard theory of ordinary differential equations that the solution to (3.17) is given by

$$(3.19) \quad U(t) = a_1 X_1 + a_2 \exp(-\lambda_2 t) X_2 + a_3 \exp(-\lambda_3 t) X_3 + a_4 \exp(-\lambda_4 t) X_4,$$

where the  $a_i$ 's are constants determined from the initial condition. So when  $t \rightarrow \infty$  the system reaches the steady state  $U(\infty) = a_1 X_1$ . It is easy to check that  $X_1 = (\gamma_1, 1, \gamma_2 b, \gamma_2/\gamma_3)^T$ .

Note that in equilibrium in (3.1)-(3.12) there hold  $C_1 = \text{const.}, \theta_0 = C_1/\gamma_1, C_2 = C_1 \gamma_2/\gamma_1,$  and  $\theta = C_1 \gamma_2/(\gamma_1 \gamma_3)$ . The constant is determined from mass conservation. Indeed, if we integrate (3.1) over  $-1 < x < 0$  and  $0 < t < T$ , using (3.3) and (3.2), we obtain

$$\int_{-1}^0 C_1(x, T) dx = \int_{-1}^0 C_1^0(x) dx + d \int_0^T \frac{\partial C_1}{\partial x}(0, t) dt,$$

and similarly for  $C_2$  in  $0 < x < b, 0 < t < T$ .

From (3.6) it follows that

$$\theta_0(T) = \theta_0^0 - d \int_0^T \frac{\partial C_1}{\partial x}(0, t) dt + \int_0^T \frac{\partial C_2}{\partial x}(0, t) dt,$$

and similarly for  $\theta(t)$  from (3.10).

Rearranging leads to

$$\bar{C}_1(T) + \bar{C}_2(T) + \theta_0(T) + \theta(T) = \bar{C}_1^0 + \theta_0^0,$$

which indeed is the law of mass conservation. Therefore if  $\lim_{T \rightarrow \infty} \bar{C}_1(T) = a$ , then

$$a + a \gamma_2 b / \gamma_1 + a / \gamma_1 + a \gamma_2 / (\gamma_1 \gamma_3) = \bar{C}_1^0 + \theta_0^0,$$

and hence

$$a = (\bar{C}_1^0 + \theta_0^0) / \left( 1 + \frac{\gamma_2 + \gamma_3 + \gamma_2 \gamma_3 b}{\gamma_1 \gamma_3} \right).$$

It can be shown that the solution (3.19) gives exactly the same answer (as it should). Therefore the coefficient of  $X_1$  in (3.19) is  $a_1 = a/\gamma_1$ .

This relationship between the model (3.1)-(3.12) and the well-mixed approximation follows from the fact that the unique solution to (3.1)-(3.12) (see § 5) converges to the unique steady state as  $t \rightarrow \infty$  and so does the solution (3.19) to (3.17)-(3.18).

The outgassing flux  $-\partial C_2/\partial x$  given by (3.8) is approximated by

$$h_2(\gamma_2 \theta_0(t) - \bar{C}_2(t)/b) = a'_2 \exp(-\lambda_2 t) + a'_3 \exp(-\lambda_3 t) + a'_4 \exp(-\lambda_4 t).$$

The  $a_i$ 's are constants. So as  $T$  gets large we have for the outgassing rate

$$\text{flux} \sim \exp(-\lambda_2 t)$$

(assuming  $a'_2 \neq 0$ ); that is,  $\lambda_2$  controls the decay of the flux. Also we have an upper estimate

$$\lambda_2 \leq \frac{1}{3} [(\gamma_1 + 1)h_1 + (\gamma_2 + 1/b)h_2 + (\gamma_3 + 1/b)h_3]$$

by noting that  $\lambda_1 + \lambda_2 + \lambda_3 + \lambda_4 = \text{tr}(A)$ .

This asymptotic behavior of the outgassing rate agrees with the experimental results (see, e.g., [12], [27], Missel and Glang [23], or [16]). Note that the decay rate is expressed in terms of the parameters but is independent of the diffusion coefficient  $d$ . Furthermore, this leads to the possibility of the experimental determination of  $\lambda_2$  from measured outgassing curves.

It is possible to consider another approximation of this type. If  $d = D_1/D_2 \gg 1$  in (3.1)–(3.12) we may consider an approximate model where the system is well mixed in  $-1 < x < 0$  only. Here we consider  $\bar{C}_1(t)$  instead of  $C_1(x, t)$  and obtain an ordinary differential equation for it. Such a model consists of three ordinary differential equations for  $\bar{C}_1(t)$ ,  $\theta_0(t)$ , and  $\theta(t)$  and a partial differential equation for  $C_2(x, t)$ ; this is similar to the system considered in Busenberg and Mahaffy [5].

**3.2. An approximation of the outgassing process.** Our model is based on three physical processes: diffusion inside the source and in the cavity, outgassing from the source through the interface into the cavity, and the contamination of the target surface. We take a closer look at outgassing. For this purpose, we assume that the effect of all of the boundaries, except for  $S_0$ , is small enough to be ignored; therefore, we put the boundaries at “infinity,” considering the source and cavity regions to be semi-infinite.

We simplify the process on the surface  $S_0$  by neglecting the surface concentration and the contaminant source, and assume that there is no volume production of the contaminant  $f_1 = 0$ . Thus we limit our study to the outgassing of the material initially trapped in the source. Under these assumptions the model (3.1)–(3.12) reduces to

$$(3.20) \quad \frac{\partial C_1}{\partial t} = d \frac{\partial^2 C_1}{\partial x^2}, \quad -\infty < x < 0, \quad t > 0,$$

$$(3.21) \quad \frac{\partial C_2}{\partial t} = \frac{\partial^2 C_2}{\partial x^2}, \quad 0 < x < \infty, \quad t > 0,$$

$$(3.22) \quad d \frac{\partial C_1}{\partial x} = \frac{\partial C_2}{\partial x}, \quad x = 0, \quad t > 0,$$

$$(3.23) \quad -d \frac{\partial C_1}{\partial x} = h(C_1 - \beta C_2), \quad x = 0, \quad t > 0,$$

$$(3.24) \quad C_1 = C_1^0, \quad -\infty < x < 0, \quad t = 0,$$

$$(3.25) \quad C_2 = 0, \quad 0 < x < \infty, \quad t = 0,$$

where  $h = (h_1 h_2 \gamma_2) / (h_1 \gamma_1 + h_2 \gamma_2)$  and  $\beta = \gamma_1 / \gamma_2$  in terms of the parameters in (3.1)–(3.12).

It is easy to verify (see Crank [9, p. 38]) that the solution to the system is given by

$$(3.26) \quad C_1(x, t) = \frac{C_1^0}{\beta + \kappa} \left\{ \beta + \kappa \left[ \operatorname{erf} \left( -\frac{x}{2\sqrt{dt}} \right) + e^{-\delta_1 x + \delta_1^2 dt} \operatorname{erfc} \left( -\frac{x}{2\sqrt{dt}} + \delta_1 \sqrt{dt} \right) \right] \right\},$$

$x \leq 0, \quad t > 0,$

$$(3.27) \quad C_2(x, t) = \frac{C_1^0}{\beta + \kappa} \left\{ \operatorname{erfc} \left( \frac{x}{2\sqrt{t}} \right) - e^{\delta_2 x + \delta_2^2 t} \operatorname{erfc} \left( \frac{x}{2\sqrt{t}} + \delta_2 \sqrt{t} \right) \right\},$$

$x \geq 0, \quad t > 0,$

where

$$(3.28) \quad \kappa = \frac{1}{\sqrt{d}}, \quad \delta_1 = \frac{h}{d} \left( 1 + \frac{\beta}{\kappa} \right), \quad \delta_2 = h(\kappa + \beta),$$

and  $\operatorname{erf}(u)$  is the error function  $2/\sqrt{\pi} \int_0^u e^{-s^2} ds$  and  $\operatorname{erfc}(u) = 1 - \operatorname{erf}(u)$ , is its complement.

The usefulness of this exact solution is apparent as it indicates the dependence of the solution on the various coefficients.

From the solution, we can easily compute the flux in the cavity:

$$\begin{aligned}
 \text{flux}(x, t) &= -\frac{\partial C_2}{\partial x}(x, t) \\
 (3.29) \qquad &= C_1^0 h \exp(\delta_2 x + \delta_2^2 t) \operatorname{erfc}\left(\frac{x}{2\sqrt{t}} + \delta_2 \sqrt{t}\right), \quad x \geq 0, \quad t > 0
 \end{aligned}$$

and the outgassing flux is obtained by setting  $x = 0$ .

A typical outgassing flux at  $x = 0$  as a function of time is depicted in Fig. 3.1 ( $d = 1, C_1^0 = 1, \beta = 1$ , and for four different values of  $h$ ).

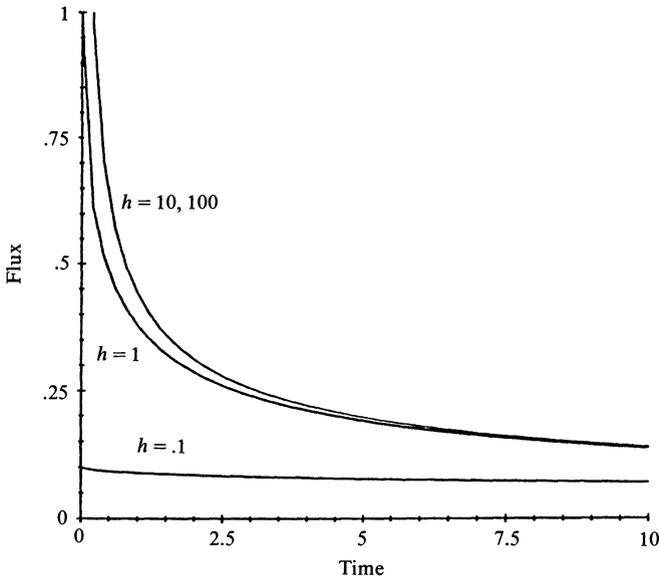


FIG. 3.1. Outgassing flux as a function of time.

From the expressions for the flux (3.29) we obtain the dependence of the process upon the parameter  $h$  as shown in Fig. 3.2 (at time  $t = 0.1$ ). It is seen that the system is sensitive to  $h$  only when  $h$  is small. This type of qualitative behavior has some important consequences from the point of view of application. This dependence on  $h$  means that when  $h$  is large there is no need to determine it with high accuracy and hence its measurements may be relatively simple. On the other hand, if it is small, then in order to obtain reasonable predictions from the model we must supply the values of  $h$  with great accuracy, which might complicate measurements and make them more expensive. In many applications the process is considered to be “diffusion controlled” (see [16], [14]), which means that  $h$  is large.

We proceed to obtain the asymptotic expansions in a number of interesting cases.

Case i.  $\beta$  fixed,  $h \rightarrow \infty$ . This is the so-called “diffusion controlled” process; the rate coefficient is very large and small deviations from equilibrium ( $C_1 = \beta C_2$ ) on  $S_0$  cause very large fluxes by which the process is driven. Thus  $C_1 \approx \beta C_2$  on  $S_0$ , and we have

$$\text{flux}(x, t) \sim \frac{\sqrt{\pi} C_1^0}{4(\kappa + \beta)\sqrt{t}} e^{-x^2/4t}, \quad x \geq 0, \quad t > 0.$$

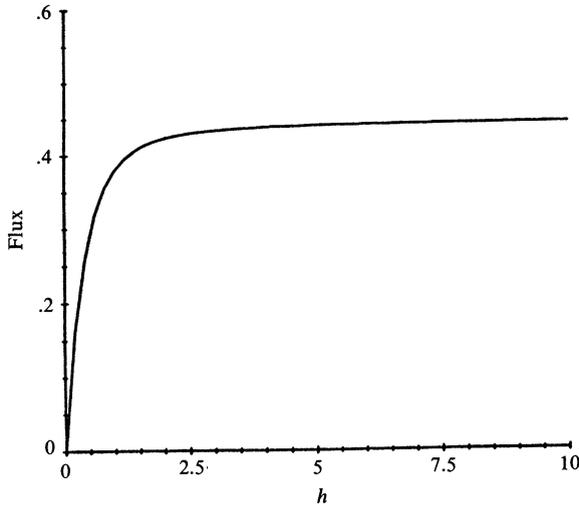


FIG. 3.2. The dependence of outgassing flux on  $h$ .

Experimental results (see, e.g., [11] or [27] and references therein) show that in many cases the outgassing flux behaves like  $1/\sqrt{t}$ , which is exactly what we get at  $x = 0$ .

Case ii.  $\beta$  fixed,  $h \rightarrow 0$ . In this case the process is driven weakly and only very large deviations from equilibrium will cause noticeable outfluxes. Since very little contaminant outgasses, the concentration  $C_2$  is very small. For small  $h$ , we have

$$\text{flux}(x, t) \sim C_1^0 h \operatorname{erfc}\left(\frac{x}{2\sqrt{t}}\right), \quad x \geq 0, \quad t > 0$$

and since the function  $\operatorname{erfc}$  decays very rapidly with  $x$ , we obtain that the molecules are concentrated near  $S_0$  where the concentration is  $O(h)$ . Under such conditions the outgassing process may take a very long time to decay.

Next we fix  $h$  and consider the asymptotic behavior with respect to  $\beta$ .

Case iii.  $h$  fixed,  $\beta \rightarrow \infty$ . In this case large concentrations of  $C_1$  are in equilibrium with small concentrations of  $C_2$ , which may indicate that there is a strong affinity of the contaminant to the material in  $\Omega_1$ . Then

$$\text{flux}(x, t) \sim \frac{\sqrt{\pi} C_1^0}{4\beta\sqrt{t}} e^{-x^2/4t}, \quad x \geq 0, \quad t > 0.$$

At  $x = 0$  the flux is  $O(1/\beta)$ .

Case iv.  $h$  fixed,  $\beta \rightarrow 0$ . There is a strong tendency for the contaminant molecules to leave  $\Omega_1$  (the source), then

$$\text{flux}(x, t) \sim C_1^0 h \exp\left(\frac{h}{\sqrt{d}}x + \frac{h^2}{d}t\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{t}} + h\sqrt{\frac{t}{d}}\right), \quad x \geq 0, \quad t > 0,$$

which is independent of  $\beta$ .

**3.3. Reduction to Volterra integral equations.** Finally we reduce system (3.1)–(3.12) to a system of Volterra integral equations and then solve this system numerically to obtain the outgassing rate. For this purpose, we introduce the following functions (the fluxes):

$$(3.30) \quad \phi_1(t) = -d \frac{\partial C_1}{\partial x}(0, t),$$

$$(3.31) \quad \phi_2(t) = -\frac{\partial C_2}{\partial x}(0, t),$$

$$(3.32) \quad \phi_3(t) = -\frac{\partial C_2}{\partial x}(b, t).$$

Now we have the following problem for  $C_1$ :

$$\frac{\partial C_1}{\partial t} = d \frac{\partial^2 C_1}{\partial x^2} + f_1, \quad -1 < x < 0, \quad t > 0,$$

$$-d \frac{\partial C_1}{\partial x} = \phi_1, \quad x = 0, \quad t > 0,$$

$$\frac{\partial C_1}{\partial x} = 0, \quad x = -1, \quad t > 0,$$

$$C_1 = C_1^0 \quad -1 < x < 0, \quad t > 0.$$

The solution to this problem has the integral representation (see Cannon [6, p. 339]):

$$(3.33) \quad \begin{aligned} C_1(x, t) = & \int_{-1}^0 \{G(-(x-\xi), dt) + G(-(x+\xi), dt)\} C_1^0(\xi) d\xi \\ & + \int_0^t \int_{-1}^0 \{G(-(x-\xi), d(t-\tau)) + G(-(x+\xi), d(t-\tau))\} f_1(\xi, \tau) d\xi d\tau \\ & - 2 \int_0^t G(-x, d(t-\tau)) \phi_1(\tau) d\tau, \quad -1 \leq x \leq 0, \quad t > 0, \end{aligned}$$

where

$$(3.34) \quad K(x, t) = \frac{1}{\sqrt{4\pi t}} e^{-x^2/4t},$$

$$(3.35) \quad G(x, t) = \sum_{m=-\infty}^{\infty} K(x+2m, t), \quad t > 0,$$

$G$  being Green's function for the problem.

The problem for  $C_2$  is

$$\frac{\partial C_2}{\partial t} = \frac{\partial^2 C_2}{\partial x^2}, \quad 0 < x < b, \quad t > 0,$$

$$-\frac{\partial C_2}{\partial x} = \phi_2, \quad x = 0, \quad t > 0,$$

$$-\frac{\partial C_2}{\partial x} = \phi_3, \quad x = b, \quad t > 0,$$

$$C_2 = 0, \quad x > 0, \quad t = 0,$$

and the solution is (see [6, p. 339])

$$(3.36) \quad C_2(x, t) = \frac{2}{b} \int_0^t \left\{ G\left(\frac{x}{b}, \frac{t-\tau}{b^2}\right) \phi_2(\tau) - G\left(\frac{x-b}{b}, \frac{t-\tau}{b^2}\right) \phi_3(\tau) \right\} d\tau, \quad 0 \leq x \leq b, \quad t > 0,$$

where  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  are to be determined.

From (3.6) and (3.10) we have

$$(3.37) \quad \theta_0(t) = \theta_0^0 + \int_0^t (\phi_1(\tau) - \phi_2(\tau) + f_0(\tau)) \, d\tau,$$

$$(3.38) \quad \theta(t) = \int_0^t \phi_3(\tau) \, d\tau.$$

Evaluating (3.33) and (3.36) on the boundaries, using the boundary conditions (3.7), (3.8), (3.11), and (3.37), (3.38) gives a system of Volterra integral equations for  $\phi_1(t)$ ,  $\phi_2(t)$ , and  $\phi_3(t)$ :

$$(3.39) \quad \begin{aligned} \phi_1(t) = & -h_1 \gamma_1 \left( \theta_0^0 + \int_0^t f_0(\tau) \, d\tau \right) + h_1 \int_{-1}^0 \{G(\xi, dt) + G(-\xi, dt)\} C_1^0(\xi) \, d\xi \\ & + h_1 \int_0^t \int_{-1}^0 \{G(\xi, d(t-\tau)) + G(-\xi, d(t-\tau))\} f_1(\xi, \tau) \, d\xi \, d\tau \\ & - h_1 \int_0^t \{[\gamma_1 + 2G(0, d(t-\tau))]\phi_1(\tau) - \gamma_1 \phi_2(\tau)\} \, d\tau, \end{aligned}$$

$$(3.40) \quad \begin{aligned} \phi_2(t) = & -h_2 \int_0^t \left\{ -\gamma_2 \phi_1(\tau) + \left( \gamma_2 + \frac{2}{b} G\left(0, \frac{t-\tau}{b^2}\right) \right) \phi_2(\tau) - \frac{2}{b} G\left(-1, \frac{t-\tau}{b^2}\right) \phi_3(\tau) \right\} \, d\tau \\ & + h_2 \gamma_2 \left( \theta_0^0 + \int_0^t f_0(\tau) \, d\tau \right), \end{aligned}$$

$$(3.41) \quad \phi_3(t) = -h_3 \int_0^t \left\{ \frac{2}{b} G\left(1, \frac{t-\tau}{b^2}\right) \phi_2 + \left( \gamma_3 + \frac{2}{b} G\left(0, \frac{t-\tau}{b^2}\right) \right) \phi_3 \right\} \, d\tau.$$

In a matrix form

$$(3.42) \quad \Phi(t) + \int_0^t \tilde{K}(t-\tau)\Phi(\tau) \, d\tau = F(t), \quad t > 0,$$

where the kernel matrix is

$$\tilde{K}(t) = \begin{pmatrix} h_1 \gamma_1 + 2h_1 G(0, dt) & -h_1 \gamma_1 & 0 \\ -h_2 \gamma_2 & h_2 \gamma_2 + \frac{2h_2}{b} G\left(0, \frac{t}{b^2}\right) & -\frac{2h_2}{b} G\left(-1, \frac{t}{b^2}\right) \\ 0 & -\frac{2h_3}{b} G\left(1, \frac{t}{b^2}\right) & h_3 \gamma_3 + \frac{2h_3}{b} G\left(0, \frac{t}{b^2}\right) \end{pmatrix},$$

$\Phi(t) = (\phi_1(t), \phi_2(t), \phi_3(t))^T$ , and the vector  $F(t)$  represents the known parts in (3.39)–(3.41). Thus the problem has been reduced to a system of integral equations of Volterra type. Once this system is solved, the solution  $\Phi(t)$  can be inserted into (3.33), (3.36) to obtain  $C_1(x, t)$ ,  $C_2(x, t)$  and into (3.37), (3.38) to get  $\theta_0(t)$ ,  $\theta(t)$ , respectively.

A numerical solution for this system of Volterra integral equations is given by a computer package in Mathlib. The figures below illustrate the solutions to these equations. Figure 3.3 gives the fluxes as functions of time. Figure 3.4 gives the total masses of contaminant on the interface ( $\theta_0$ ) and on the target ( $\theta$ ). In these two figures all the parameters are chosen as 1 with the initial concentrations  $C_0^0 = 1$ ,  $\theta_0^0 = 0.5$  and  $f_1 \equiv 0$ ,  $f_0 \equiv 0$ .

**4. Numerical solutions.** In this section we describe an algorithm for the numerical solution of problem (2.8)–(2.20); we outline the computer program based on this

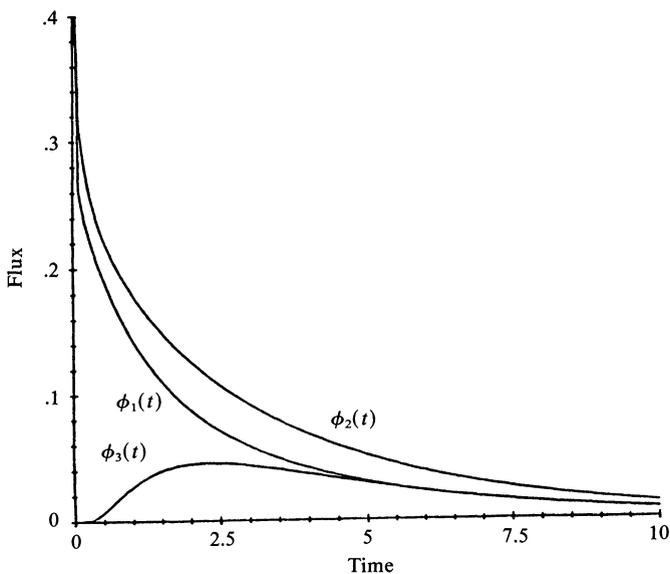


FIG. 3.3. Fluxes as functions of time.

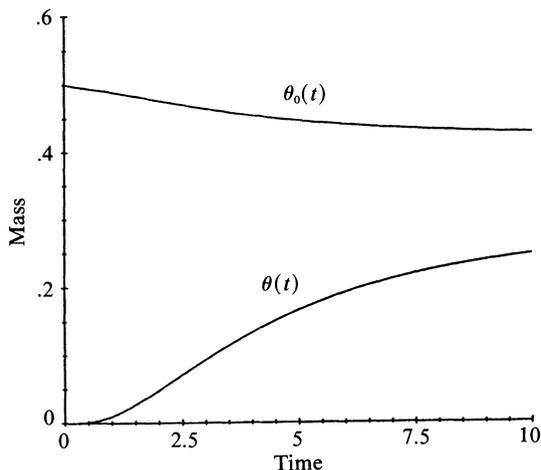


FIG. 3.4. Total masses as functions of time.

algorithm and present some examples of numerical results. These numerical solutions show the behavior of the model and its dependence on the data. Eventually, these results should be compared to experimental data and used to predict the contamination process in the relevant physical environments.

The model described by (2.8)-(2.20) is an evolution problem. We wish to solve for  $C_1$ ,  $C_2$ ,  $\theta_0$ , and  $\theta$  as functions of time and space, so we first discretize the system with respect to the time variable and then, at each timestep, solve the resulting problem with respect to the spatial variables. This is the standard marching procedure.

The discretization is as follows. Let  $t = t_n = n\delta t$ ,  $n = 0, 1, 2, \dots$  where  $\delta t$  is the timestep. We denote the functions evaluated at each time  $t_n$  as  $C_{1,n}(x, y) = C_1(x, y, t_n)$ ,

$C_{2,n}(x, y) = C_2(x, y, t_n)$ ,  $\theta_{0,n}(y) = \theta_0(y, t_n)$ , and  $\theta_n(y) = \theta(y, t_n)$ . We use the Crank-Nicolson discretization (see, e.g., Smith [31] or Issacson and Keller [21]) for evaluating  $C_1$  and  $C_2$  because of its unconditional stability. For  $\theta_0$  and  $\theta$  we use fully implicit discretization. Such discretization of (2.8)–(2.20) with respect to time leads to the following system:

$$(4.1) \quad C_{1,n} = C_{1,n-1} + \frac{\delta t}{2} (d\Delta C_{1,n}) + \frac{\delta t}{2} (d\Delta C_{1,n-1}) + \delta t f_{1,n} \quad \text{in } \Omega_1,$$

$$(4.2) \quad C_{2,n} = C_{2,n-1} + \frac{\delta t}{2} (\Delta C_{2,n-1} - \vec{v} \cdot \nabla C_{2,n-1}) + \frac{\delta t}{2} (\Delta C_{2,n} - \vec{v} \cdot \nabla C_{2,n}) \quad \text{in } \Omega_2,$$

$$(4.3) \quad -\frac{\partial C_{2,n}}{\partial n} + v_n C_{2,n} = h_0 C_{2,n} \quad \text{on } S_2,$$

$$(4.4) \quad \theta_{0,n} = \theta_{0,n-1} - \delta t \left( d \frac{\partial C_{1,n}}{\partial x} + \frac{\partial C_{2,n}}{\partial x} - v_x C_{2,n} \right) + \delta t f_{0,n} \quad \text{on } S_0,$$

$$(4.5) \quad -d \frac{\partial C_{1,n}}{\partial x} = h_1 (C_{1,n} - \gamma_1 \theta_{0,n}) \quad \text{on } S_0,$$

$$(4.6) \quad -\frac{\partial C_{2,n}}{\partial x} + v_x C_{2,n} = h_2 (\gamma_2 \theta_{0,n} - C_{2,n}) \quad \text{on } S_0,$$

$$(4.7) \quad \theta_n = \theta_{n-1} - \delta t \left( \frac{\partial C_{2,n}}{\partial x} + v_x C_{2,n} \right) \quad \text{on } S_3,$$

$$(4.8) \quad -\frac{\partial C_{2,n}}{\partial x} + v_x C_{2,n} = H(C_{2,n}, \theta_n) \quad \text{on } S_3,$$

$$(4.9) \quad \frac{\partial C_{1,n}}{\partial n} = 0 \quad \text{on } S_1,$$

$n = 1, 2, \dots$ , where in addition  $C_{1,0} = C_1^0$  in  $\Omega_1$ ,  $\theta_{0,0} = \theta_0^0$  on  $S_0$ ,  $C_{2,0} = 0$  in  $\Omega_2$ ,  $\theta_0 = 0$  on  $S_3$ , and  $\partial C_{1,n} / \partial n = 0$  on  $S_1$ . Here we set  $f_{1,n} = f_1(x, y, t_n)$  in  $\Omega_1$  and  $f_{0,n} = f_0(y, t_n)$  on  $S_0$ .

Since the system is coupled, we use an iterative method for solving it at each timestep. We start with known values from the previous timestep and compute the new iterative values  $C_1$  and  $C_2$  using previous values of  $\theta_0$  and  $\theta$ . Then we re-compute  $\theta_0$  and  $\theta$  using the new values of  $C_1$  and  $C_2$ . We continue these iterations until the difference between successive iterative values for  $\theta_0$  and  $\theta$  is sufficiently small. This is sufficient because, by the maximum principle for elliptic equations, the iterative sequences for  $C_1$  and  $C_2$  converge once the iterative sequences for  $\theta_0$  and  $\theta$  converge.

The iteration process consists of the following steps where we let the superscript  $m$  be the iteration number and let quantities without superscripts represent the final results from the previous timestep. Then for  $m = 1, 2, 3, \dots$ , we get the following steps.

*Step 1.* Calculate  $C_{1,n}^m$  from

$$(4.10) \quad C_{1,n}^m - \frac{\delta t}{2} d\Delta C_{1,n}^m = C_{1,n-1} + \frac{\delta t}{2} d\Delta C_{1,n-1} + \delta t f_{1,n} \quad \text{in } \Omega_1,$$

$$(4.11) \quad \frac{\partial}{\partial n} C_{1,n}^m = 0 \quad \text{on } S_1,$$

$$(4.12) \quad -d \frac{\partial}{\partial x} C_{1,n}^m = h_1 C_{1,n}^m - \gamma_1 h_1 \theta_{0,n}^{m-1} \quad \text{on } S_0.$$

Step 2. Calculate  $C_{2,n}^m$  from

$$(4.13) \quad C_{2,n}^m - \frac{\delta t}{2} (\Delta C_{2,n}^m - \vec{v} \cdot \nabla C_{2,n}^m) = C_{2,n-1} + \frac{\delta t}{2} (\Delta C_{2,n-1} - \vec{v} \cdot \nabla C_{2,n-1}) \quad \text{in } \Omega_2,$$

$$(4.14) \quad -\frac{\partial}{\partial n} C_{2,n}^m + v_n C_{2,n}^m = h_0 C_{2,n}^m \quad \text{on } S_2,$$

$$(4.15) \quad -\frac{\partial}{\partial x} C_{2,n}^m + (v_x + h_2) C_{2,n}^m = h_2 \gamma_2 \theta_{0,n}^{m-1} \quad \text{on } S_0,$$

$$(4.16) \quad -\frac{\partial}{\partial x} C_{2,n}^m + v_x C_{2,n}^m = H(C_{2,n}^{m-1}, \theta_n^{m-1}) \quad \text{on } S_3.$$

Step 3. Calculate  $\theta_{0,n}^m$  from

$$(4.17) \quad (1 + \delta t (h_2 \gamma_2 + h_1 \gamma_1)) \theta_{0,n}^m = \theta_{0,n-1} + \delta t (h_2 C_{2,n}^m + h_1 C_{1,n}^m) \quad \text{on } S_0,$$

where we use (4.5) and (4.6) in (4.4).

Step 4. Calculate  $\theta_n^m$  from

$$(4.18) \quad \theta_n^m = \theta_{n-1} + \delta t H(C_{2,n}^m, \theta_n^{m-1}) \quad \text{on } S_3,$$

where we substitute (4.8) in (4.7).

Step 5. Calculate

$$\max |\theta_{0,n}^m - \theta_{0,n}^{m-1}| \quad \text{and} \quad \max |\theta_n^m - \theta_n^{m-1}|.$$

The condition for continued iteration is based on these maxima. If the maxima are less than  $\varepsilon$ , the accuracy parameter, then we stop the iterations, set  $C_{1,n} = C_{1,n}^m$ ,  $C_{2,n} = C_{2,n}^m$ ,  $\theta_{0,n} = \theta_{0,n}^m$ , and  $\theta_n = \theta_n^m$ , and move on to the next time  $t = t_{n+1} = (n + 1) \delta t$ . Otherwise we repeat Steps 1-5 for the iteration  $m + 1$ .

It is clear that the calculations of  $\theta_{0,n}^m$ , (4.17) and  $\theta_n^m$ , (4.18) are straightforward; they involve only the evaluation of algebraic expressions. However, the evaluation of  $C_{1,n}^m$  and  $C_{2,n}^m$  involves the solution of two elliptic partial differential equations. To solve these problems numerically we use the software package ELLPACK [25].

We present the numerical solutions to some problems to show the typical behavior of the model. We choose the sorption function  $H(C_2, \theta) = h_3 C_2 - \gamma_3 h_3 \theta$  on  $S_3$ , which is a simplification of (2.4), essentially choosing  $\theta_{\max}$  large. The problem is considered in two dimensions only.

In the examples below we choose the parameters to be  $d = 1$ ,  $\gamma_1 = \gamma_2 = \gamma_3 = 1$ , and  $h_1 = h_3 = 1$ . No source functions, i.e.,  $f_0 = f_1 = 0$ , initially  $C_2^0 = \theta^0 = 0$ , i.e., the cavity and the target are empty of contaminant and no convection in  $\Omega_2$ , i.e.,  $\vec{v} = 0$ .

Both domains  $\Omega_1(0 < x < 1, 0 < y < 1)$  and  $\Omega_2(1 < x < 2, 0 < y < 1)$  were divided into a regular mesh of size  $\delta x = \delta y = 0.1$  and  $S_0$  and  $S_3$  were divided into steps of size  $\delta y = 0.1$ . It was found that the timestep  $\delta t = 0.025$  gave satisfactory results.

*Example 1.* In the first example we took  $C_1^0 = 10$  and  $\theta_0^0 = 10$  (so the process evolves quickly) and  $h_0 = h_2 = 1$ .

The time evolution of the concentrations (for  $y = 0.5$ , i.e., at the middle of the system) as a function of  $x$  is depicted in Fig. 4.1. The cavity is represented as  $0 < x < 1$  where  $C_1$  is seen to be a decreasing function of time for  $0 < t < 6$  (arbitrary units).

The concentration  $\theta_0 = \theta(y = 0.5)$  is also a decreasing function of time. On the other hand,  $C_2$  is a function of  $x$  and  $t$  ( $y = 0.5$ ) and is an increasing function initially as the contaminant desorbs from  $S_0$  into  $\Omega_2$  and then it is decreasing as a consequence

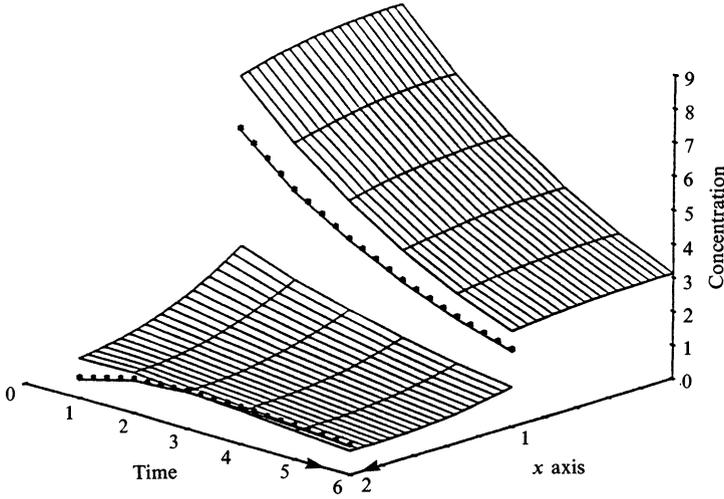


FIG. 4.1. Example 1. The time evolution of the system. The source  $0 < x < 1$ , the interface at  $x = 1$ , the cavity  $1 < x < 2$ , and the target at  $x = 2$ .

of the loss of material through the boundary  $S_2$ . It is interesting to note that initially the contaminant concentration on the target  $\theta$  is less than  $C_2$  on the target ( $x = 2$ ) and deposition takes place on the target; at about  $t = 2.5$  the level of  $C_2$  decreases below that of  $\theta$  and desorption from the surface starts.

This behavior can be seen clearly in Fig. 4.2 where the concentrations  $C_1$ ,  $\theta_0$ ,  $C_2$ , and  $\theta$  are given on their domains for fixed time  $t = 1.0$ .

Note that on  $x = 0$ ,  $C_1 \neq \theta_0$  and  $C_2 \neq \theta_0$  as a result of our assumption. Finally, for large  $t$  the system tends to zero concentration and there is total desorption from the target.

*Example 2.* In this example we compared the solution with  $h_0 = 100$  to the solution where the boundary condition (2.13) is replaced by  $C_2 = 0$  on  $S_2$ . Also  $C_1^0 = 10$ ,  $\theta_0^0 = 10$ , and the rest of the coefficients as above. The comparison is given in Table 4.1 where the maximum of the differences of the solutions at  $t = 5.0$  is given. The predictions on the source differ by 9.1 percent at most.

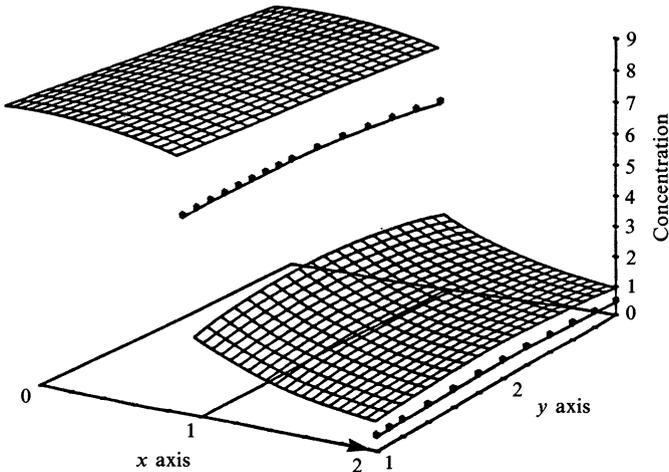


FIG. 4.2. Example 1, at  $t = 1.0$ .

TABLE 4.1

	Absolute difference	% difference
$C_1$	1.206E-02	1.9
$C_2$	7.470E-03	6.9
$\theta_0$	1.051E-02	2.7
$\theta$	1.730E-03	9.1

Comparison of the solutions with  $h_0 = 100$  to the solution where  $C_2 = 0$  on  $S_2$  at  $t = 5.0$ .

The time evolution of the problem with  $C_2 = 0$  on  $S_2$  is given in Fig. 4.3.

*Example 3.* In order to simulate chemisorption on the target, that is a process by which desorption is very slow (the molecules are chemically bonded to the surface), we choose  $\gamma_3 = 0.01$  and the rest as in Example 1. The time evolution of the system is given in Fig. 4.4. Clearly, there is a large buildup of contamination on the target even when the concentration in the cavity is small. It can be seen more clearly in Fig. 4.5 where the concentrations are given at time  $t = 6.0$ .

**5. Uniqueness.** In this section, we prove the uniqueness of the solution to the general model (§ 2), which includes surface diffusion on the source-cavity interface  $S_0$  and on the target  $S_3$  (see Fig. 2.1). For simplicity, we consider the model in two space dimensions. Thus the problem we consider is the following system of evolution equations:

$$(5.1) \quad \frac{\partial C_1}{\partial t} = \nabla \cdot (D_1 \nabla C_1) + f_1(C_1) \quad \text{in } \Omega_1, \quad t > 0,$$

$$(5.2) \quad \frac{\partial C_2}{\partial t} = \nabla \cdot (D_2 \nabla C_2 - \vec{v} C_2) \quad \text{in } \Omega_2, \quad t > 0,$$

$$(5.3) \quad \frac{\partial \theta_0}{\partial t} = \frac{\partial}{\partial y} \left( d_0 \frac{\partial \theta_0}{\partial y} \right) + \left( -D_1 \frac{\partial C_1}{\partial n} \right) - \left( -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 \right) + f_0(\theta_0), \quad \text{on } S_0, \quad t > 0,$$

$$(5.4) \quad \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial y} \left( d \frac{\partial \theta}{\partial y} \right) + \left( -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 \right) \quad \text{on } S_3, \quad t > 0,$$

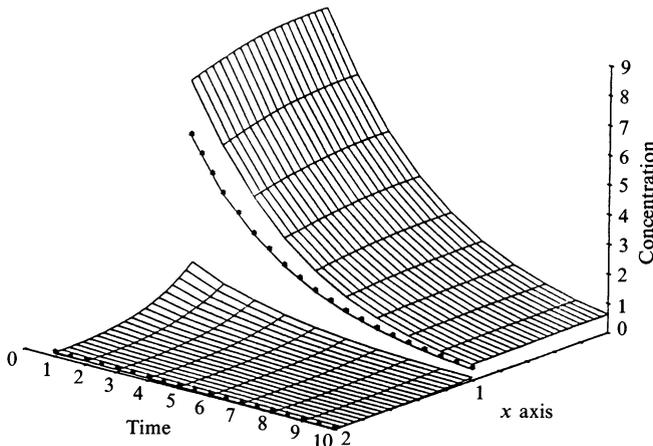


FIG. 4.3. Example 2, with  $C_2 = 0$  on  $S_2$ .

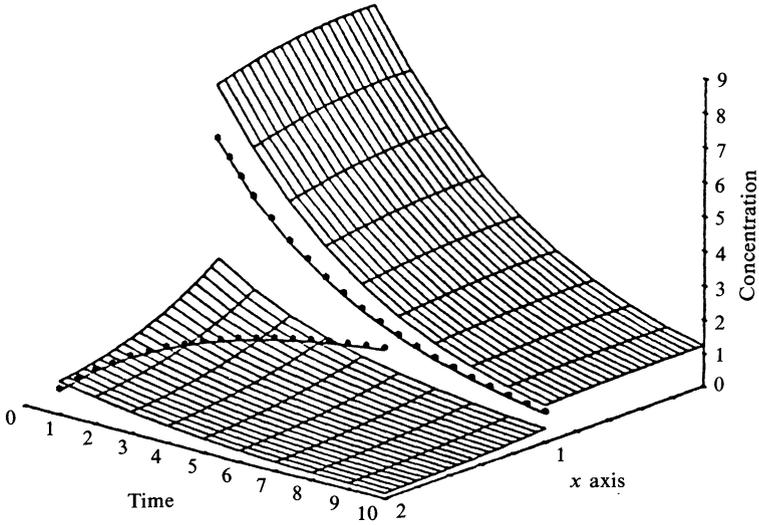


FIG. 4.4. Example 3, with  $\gamma_3 = 0.01$ .

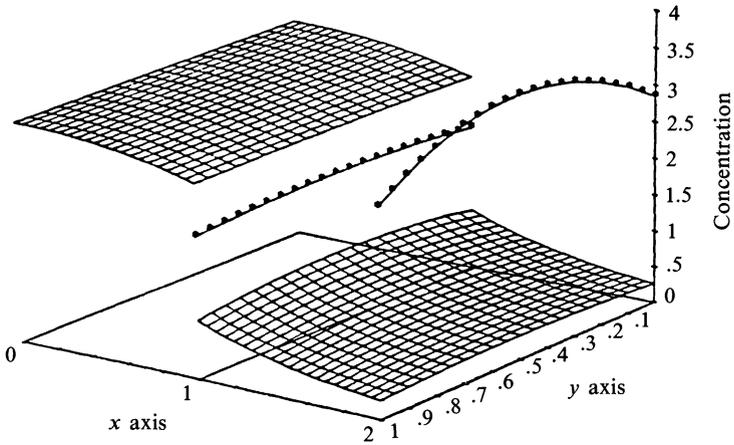


FIG. 4.5. Example 3, at  $t = 6.0$ .

with boundary conditions

$$(5.5) \quad -D_1 \frac{\partial C_1}{\partial n} = \begin{cases} 0 & \text{on } S_1, \\ H_1(C_1 - \gamma_1 \theta_0) & \text{on } S_0, \end{cases} \quad t > 0,$$

$$(5.6) \quad -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 = \begin{cases} H_2(\gamma_2 \theta_0 - C_2) & \text{on } S_0, \\ H_0(C_2) & \text{on } S_2, \\ -K_1(\theta) + K_2(\theta) C_2 & \text{on } S_3, \end{cases} \quad t > 0,$$

$$(5.7) \quad d_0 \frac{\partial \theta_0}{\partial y} = 0 \quad \text{on } \partial S_0, \quad d \frac{\partial \theta}{\partial y} = 0 \quad \text{on } \partial S_3, \quad t > 0,$$

and initial conditions

$$(5.8) \quad \begin{aligned} C_1 &= C_1^0(x, y) \quad \text{in } \Omega_1, & C_2 &= C_2^0(x, y) \quad \text{in } \Omega_2, \\ \theta_0 &= \theta_0^0(y) \quad \text{on } S_0, & \theta &= \theta^0(y) \quad \text{on } S_3, \end{aligned} \quad \text{at } t = 0.$$

The notation is the same as in § 2 and, in addition,  $d_0$  and  $d$  are the diffusion coefficients on  $S_0$  and  $S_3$ , respectively. The source functions,  $f_1$  and  $f_0$ , depend on the concentrations  $C_1$  and  $\theta_0$ , respectively.  $H_0$ ,  $H_1$ , and  $H_2$  are generalizations of the boundary conditions. Moreover, we allow spatial dependence for  $\gamma_1$  and  $\gamma_2$ .

We will need the following assumptions:

- (A1)  $D_1(x, y)$  and  $D_2(x, y)$  are continuous in  $\bar{\Omega}_1$  and  $\bar{\Omega}_2$ , respectively;  $d_0(y)$  and  $d(y)$  are continuous on  $0 \leq y \leq b$  and they satisfy

$$0 < \mu \leq D_1, D_2 \leq M \quad \text{and} \quad 0 \leq d_0, d \leq M$$

for some constants  $\mu$  and  $M$ .

- (A2)  $\gamma_1$  and  $\gamma_2$  are continuously differentiable on  $0 \leq y \leq 1$  and satisfy

$$0 < \mu_1 \leq \gamma_1, \gamma_2 \quad \text{and} \quad \gamma_1, \gamma_2, \left| \frac{d\gamma_1}{dy} \right|, \left| \frac{d\gamma_2}{dy} \right| \leq M_1$$

for some constants  $\mu_1$  and  $M_1$ .

- (A3)  $\vec{v}(x, y)$  is a smooth vector field, bounded by  $M$  on  $\bar{\Omega}_2$ , and

$$v_n(x, y) = \vec{v}(x, y) \cdot \vec{n} \geq 0 \quad \text{on } \partial\Omega_2,$$

$$\nabla \cdot \vec{v} = 0 \quad \text{in } \Omega_2,$$

where  $n$  is the normal on  $\partial\Omega_2$  (outward on  $S_2 \cup S_3$  and inward to  $\Omega_2$  on  $S_0$ ).

- (A4) The nonlinear sorption rate functions  $H_0(\cdot)$ ,  $H_1(\cdot)$ ,  $H_2(\cdot)$ ,  $K_1(\cdot)$ , and  $-K_2(\cdot)$  are nondecreasing and

$$K_1(0) = 0 \quad \text{and} \quad H_k(0) = 0 \quad (k = 0, 1, 2).$$

$K_1$  and  $K_2$  are Lipschitz continuous with Lipschitz constant  $L$  and

$$0 < \mu_2 \leq K_2(s) \leq M_2, \quad s \in \mathbf{R},$$

for some constants  $\mu_2$  and  $M_2$ .

- (A5)  $f_0(\cdot)$  and  $f_1(\cdot)$  are Lipschitz continuous with Lipschitz constant  $L$ .

- (A6)  $C_1^0$  is continuous on  $\bar{\Omega}_1$ ,  $C_2^0$  is continuous on  $\bar{\Omega}_2$ ,  $\theta_0^0$  and  $\theta^0$  are continuous on  $[0, b]$ .

The question of existence of solutions to this problem are considered in Busenberg, Fang, and Shillor [4]. We remark that some of the assumptions can be weakened when considering weak solutions. Considering smooth solutions, we have the following theorem.

**THEOREM (uniqueness).** *Under the assumptions (A1)–(A6), the problem (5.1)–(5.8) has at most one bounded solution  $u = (C_1, C_2, \theta_0, \theta)$ .*

*Proof.* Assume that the system admits two smooth solutions  $u^{(1)} = (C_1^{(1)}, C_2^{(1)}, \theta_0^{(1)}, \theta^{(1)})$  and  $u^{(2)} = (C_1^{(2)}, C_2^{(2)}, \theta_0^{(2)}, \theta^{(2)})$ . Let  $u = u^{(1)} - u^{(2)}$ , i.e.,

$$(5.9) \quad C_1 = C_1^{(1)} - C_1^{(2)}, \quad C_2 = C_2^{(1)} - C_2^{(2)}, \quad \theta_0 = \theta_0^{(1)} - \theta_0^{(2)}, \quad \theta = \theta^{(1)} - \theta^{(2)}.$$

We show that  $u = 0$ , i.e.,  $C_1 = C_2 = \theta_0 = \theta = 0$ .

From (5.1)–(5.8), it follows that  $u = (C_1, C_2, \theta_0, \theta)$  satisfies the following problem:

$$(5.10) \quad \frac{\partial C_1}{\partial t} = \nabla \cdot (D_1 \nabla C_1) + \delta f_1 \quad \text{in } \Omega_1, \quad t > 0,$$

$$(5.11) \quad \frac{\partial C_2}{\partial t} = \nabla \cdot (D_2 \nabla C_2 - \vec{v} C_2) \quad \text{in } \Omega_2, \quad t > 0,$$

$$(5.12) \quad \frac{\partial \theta_0}{\partial t} = \frac{\partial}{\partial y} \left( d_0 \frac{\partial \theta_0}{\partial y} \right) + \left( -D_1 \frac{\partial C_1}{\partial n} \right) - \left( -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 \right) + \delta f_0 \quad \text{on } S_0, \quad t > 0,$$

$$(5.13) \quad \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial y} \left( d \frac{\partial \theta}{\partial y} \right) + \left( -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 \right) \quad \text{on } S_3, \quad t > 0,$$

with boundary conditions

$$(5.14) \quad -D_1 \frac{\partial C_1}{\partial n} = \begin{cases} 0 & \text{on } S_1, \\ \delta H_1 & \text{on } S_0, \end{cases} \quad t > 0,$$

$$(5.15) \quad -D_2 \frac{\partial C_2}{\partial n} + v_n C_2 = \begin{cases} \delta H_2 & \text{on } S_0, \\ \delta H_0 & \text{on } S_2, \\ -\delta K_1 + C_2^{(1)} \delta K_2 + K_2(\theta^{(2)}) C_2^{(2)} & \text{on } S_3, \end{cases} \quad t > 0,$$

$$(5.16) \quad d_0 \frac{\partial \theta_0}{\partial y} = 0 \quad \text{on } \partial S_0, \quad \frac{\partial \theta}{\partial y} = 0 \quad \text{on } \partial S_3, \quad t > 0,$$

and homogeneous initial conditions

$$(5.17) \quad C_1 = C_2 = \theta_0 = \theta = 0, \quad t = 0,$$

where we use the notation  $\delta g$  for a function  $g(s)$  to denote the difference

$$\delta g = g(s^{(1)}) - g(s^{(2)}),$$

for given  $s^{(1)}$  and  $s^{(2)}$ .

Next we obtain energy inequalities for  $C_1$ ,  $C_2$ ,  $\theta_0$ , and  $\theta$  using a standard technique; that is, we multiply (5.10) by  $C_1$ , integrate over  $\Omega_1 \times [0, t]$ , and use the boundary conditions (5.14). The result is

$$(5.18) \quad \begin{aligned} \frac{1}{2} \int_{\Omega_1} C_1^2 + \mu \int_0^t \int_{\Omega_1} |\nabla C_1|^2 &\leq \int_0^t \int_{S_0} (-\delta H_1) C_1 + \int_0^t \int_{\Omega_1} C_1 \delta f_1 \\ &\leq \int_0^t \int_{S_0} (-\delta H_1) C_1 + L \int_0^t \int_{\Omega_1} |C_1|^2, \end{aligned}$$

where (A1) and (A5) were used, and similarly,

$$\begin{aligned} &\frac{1}{2} \int_{\Omega_2} C_2^2 + \int_0^t \int_{\Omega_2} D_2 |\nabla C_1|^2 \\ &= \int_0^t \int_{\Omega_2} \nabla C_2 \cdot (\vec{v} C_2) \\ &\quad + \int_0^t \left\{ \int_{S_0} C_2 \delta H_2 + \int_{S_2} C_2 (-\delta H_0) + \int_{S_3} C_2 [\delta K_1 - C_2^{(1)} \delta K_2 - K_2(\theta^{(2)}) C_2] \right\}. \end{aligned}$$

By Young’s inequality,

$$|\nabla C_2 \cdot (\vec{v}C_2)| \leq \mu |\nabla C_2|^2 + \frac{1}{4\mu} |\vec{v}|^2 |C_2|^2,$$

where  $\mu$  is as in (A1). Therefore,

$$(5.19) \quad \frac{1}{2} \int_{\Omega_2} C_2^2 \leq \frac{M^2}{4\mu} \int_0^t \int_{\Omega_2} |C_2|^2 + \int_0^t \{\text{boundary integrals}\}.$$

For  $\theta_0$  and  $\theta$ , we have the “weighted” energy inequalities, which are obtained by multiplying (5.12) by  $\gamma_1\theta_0$  and integrating over  $S_0 \times [0, t]$ :

$$\begin{aligned} \frac{1}{2} \int_{S_0} \gamma_1 \theta_0^2 &= - \int_0^t \int_{S_0} d_0 \frac{\partial}{\partial y} (\gamma_1 \theta_0) \frac{\partial \theta_0}{\partial y} + \int_0^t \int_{S_0} \gamma_1 \theta_0 (\delta H_1 - \delta H_2) \\ &= - \int_0^t \int_{S_0} d_0 \gamma_1 \left( \frac{\partial \theta_0}{\partial y} \right)^2 - \int_0^t \int_{S_0} d_0 \frac{d\gamma_1}{dy} \theta_0 \frac{\partial \theta_0}{\partial y} \\ &\quad + \int_0^t \int_{S_0} \gamma_1 \theta_0 (\delta H_1 - \delta H_2). \end{aligned}$$

Again,

$$\left| \theta_0 \frac{\partial \theta_0}{\partial y} \right| \leq \frac{\varepsilon_1}{2} \left( \frac{\partial \theta_0}{\partial y} \right)^2 + \frac{1}{2\varepsilon_1} |\theta_0|^2,$$

with

$$\varepsilon_1 = \frac{2\mu_1}{M_1}.$$

Hence, by (A2), we have

$$(5.20) \quad \frac{\mu_1}{2} \int_{S_0} \theta_0^2 \leq \frac{MM_1^2}{4\mu_1} \int_0^t \int_{S_0} \theta_0^2 + \int_0^t \int_{S_0} \gamma_1 \theta_0 (\delta H_1 - \delta H_2).$$

Similarly,

$$(5.21) \quad \frac{\mu_1}{2} \int_{S_3} \theta^2 \leq \frac{MM_1^2}{4\mu_1} \int_0^t \int_{S_3} \theta^2 + \int_0^t \int_{S_3} \gamma_2 \theta [-\delta K_1 + \delta K_2 C_2^{(2)} + K_2(\theta^{(1)}) C_2].$$

Now define

$$E(t) = \frac{1}{2} \int_{\Omega_1} C_1^2 + \frac{1}{2} \int_{\Omega_2} C_2^2 + \frac{\mu_1}{2} \int_{S_0} \theta_0^2 + \frac{\mu_1}{2} \int_{S_3} \theta^2.$$

Then from (5.18)–(5.21), we have

$$\begin{aligned} (5.22) \quad E(t) &\leq L \int_0^t \int_{\Omega_1} C_1^2 + \frac{M^2}{4\mu} \int_0^t \int_{\Omega_2} C_2^2 + \frac{MM_1^2}{4\mu_1} \int_0^t \int_{S_0} \theta_0^2 + \frac{MM_1^2}{4\mu_1} \int_0^t \int_{S_3} \theta^2 \\ &\quad + \int_0^t \int_{S_0} [-(C_1 - \gamma_1 \theta_0) \delta H_1 - (\gamma_2 \theta - C_2) \delta H_2] + \int_0^t \int_{S_2} (-C_2 \delta H_0) \\ &\quad + \int_0^t \int_{S_3} (C_2 - \gamma_2 \theta) [\delta K_1 - C_2^{(2)} \delta K_2 - K_2(\theta^{(1)}) C_2]. \end{aligned}$$

The surface integrals satisfy

$$\int_{S_0} \leq 0 \quad \text{and} \quad \int_{S_2} \leq 0,$$

since  $H_0(\cdot)$ ,  $H_1(\cdot)$ , and  $H_2(\cdot)$  are nondecreasing and therefore, for any  $s_1$  and  $s_2$ ,

$$(s_1 - s_2)\delta H_i = (s_1 - s_2)[H_i(s_1) - H_i(s_2)] \geq 0.$$

Note that for a fixed  $T > 0$ ,  $|C_2^{(2)}|$  is bounded in  $\bar{\Omega}_2 \times [0, T]$  by some constant  $M_T$  depending on  $T$ . Then on  $S_3 \times [0, t] (t \leq T)$  by (A2) and (A4) we have the following estimates:

$$\begin{aligned} C_2(\delta K_1 - C_2^{(2)}\delta K_2) &\leq L(1 + M_T)|\theta||C_2|, \\ -K_2(\theta^{(2)})|C_2|^2 &\leq -\mu_2|C_2|^2, \quad -\gamma_2\theta\delta K_1 \leq 0, \\ \gamma_2\theta(C_2^{(2)}\delta K_2 - K_2(\theta^{(2)})C_2) &\leq M_1(M_T L|\theta| + M_2|C_2^{(2)}|)|\theta|. \end{aligned}$$

Therefore the integral over  $S_3$  in (5.22) satisfies

$$\begin{aligned} \int_{S_3} &\leq \int_{S_3} \{-\mu_2|C_2|^2 + [M_1M_2 + (1 + M_T)L]|\theta||C_2| + M_1M_T L|\theta|^2\} \\ &\leq \left\{ M_1M_T L + \frac{(M_1M_2 + (1 + M_T)L)^2}{4\mu_2} \right\} \int_{S_3} |\theta|^2. \end{aligned}$$

Hence (5.22) becomes

$$E(t) \leq \Lambda \int_0^t E(\tau) d\tau \quad \text{for } t \in [0, T],$$

where  $\Lambda > 0$  is an appropriate constant. Then by Gronwall's inequality,

$$0 \leq E(t) \leq E(0) e^{\Lambda t},$$

but we know that  $E(0) = 0$  from (5.9), hence  $E(t) \equiv 0$  for  $0 \leq t \leq T$ . This implies that

$$C_1 \equiv C_2 \equiv \theta_0 \equiv \theta \equiv 0, \quad 0 \leq t \leq T,$$

for any  $T > 0$ . □

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