

Stochastic sensitivity analysis in chemical kinetics

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The stochastic sensitivity analysis problem in chemical kinetics is defined as determining the probability density function (pdf) of the concentrations given probability density functions for the parameters and initial conditions. The joint concentration parameter pdf is found to satisfy the equation $(\partial p/\partial t) + \text{div}(Fp) = 0$, where the system dynamics are given by $\dot{x} = F(x)$. The properties of the solution of this equation are studied, and the approach is applied to analyze the sensitivity of the kinetics of the photolysis of a mixture of carbon monoxide, nitrogen dioxide, nitric oxide, and water in air to uncertainties in the initial concentrations of the nitrogen oxides and in the values of two photolysis rate constants. Comparisons to other sensitivity analysis approaches are discussed.

I. INTRODUCTION

The concentrations of species participating in a set of chemical reactions are governed by the vector ordinary differential equation¹

$$dz/dt = f(z; k), \quad (1)$$

$$z(0) = z_0, \quad (2)$$

where z is the n vector of concentrations, and k is an m vector of time-independent parameters, such as rate constants, activation energies, etc. If k_j is a rate constant, for example, there may exist a number of experimental determinations of k_j that lead to a range of values within which k_j should lie. Usually one selects a preferred value of k_j , call it \bar{k}_j , from among the available values, although there will be some uncertainty as to whether \bar{k}_j is, in fact, the "true" value of k_j . The sensitivity analysis problem can be stated in a general way: Given a degree of uncertainty in k , and perhaps also in z_0 , what is the resulting uncertainty in $z(t)$?

Much of the effort in sensitivity analysis has been devoted to developing techniques for calculating the first-order sensitivity coefficients $(\partial z_i/\partial k_j)_{\bar{k}}$.²⁻⁶ Although the sensitivity coefficients provide direct information on the effect of a small variation in each parameter about its nominal value on $z(t)$, they do not necessarily indicate the effect of large, simultaneous parameter variations on $z(t)$. An alternative to assessing sensitivity via the first-order sensitivity coefficients is a class of methods in which simultaneous variations of arbitrary magnitude in k are used to determine the contributions of individual parameter uncertainties to the overall uncertainty in $z(t)$.⁷⁻¹² Both types of approaches are also applicable to assessing the sensitivity to uncertain initial conditions.

If the stochastic nature of the parameter vector k and the initial condition vector z_0 can be expressed in terms of probability density functions (pdf) $p_k(k)$ and $p_0(z)$, then the sensitivity analysis can be posed in terms of computing the pdf of $z(t)$. This approach can be termed the stochastic sensitivity analysis problem.

In this paper we develop the concepts of the stochastic

sensitivity analysis problem. It will be important to keep in mind that this approach to sensitivity analysis is feasible only when the parameter and initial condition uncertainties can be identified in terms of pdf's. Section II contains the derivation of the basic equation governing the pdf of $z(t)$, and Sec. III is devoted to a discussion of the solution of that equation. In Sec. IV we consider an example consisting of a set of reactions representing the photolysis of a mixture of CO, NO₂, NO, H₂O, and air. The relationship of the stochastic sensitivity analysis to other approaches is discussed in Sec. V.

II. STOCHASTIC SENSITIVITY ANALYSIS THEORY

Let us define the $(n+m)$ -vector x by $(z_1, \dots, z_n, k_1, \dots, k_m)$, where x is governed by

$$dx/dt = F(x), \quad (3)$$

$$x(0) = x_0, \quad (4)$$

with $F(x) = (f_1, \dots, f_n, 0, \dots, 0)$ and $x_0 = (z_{10}, \dots, z_{n0}, k_{10}, \dots, k_{m0})$. Therefore, it suffices to consider the system of equations (3) and (4) in which the first n elements of x , x_1, x_2, \dots, x_n , are the concentrations and the last m elements of x , x_{n+1}, \dots, x_{n+m} , are the parameters.

Given Eqs. (1) and (2), if f is sufficiently smooth, there exists an $\eta > 0$ and a smooth function $\phi: T \times X \rightarrow X$, where $T = (-\eta, \eta)$, and X is an open set in R^n , such that¹³

$$\frac{\partial \phi}{\partial t}(t, x) = F[\phi(t, x)], \quad t \in T, \quad x \in X, \quad (5)$$

$$\phi(0, x) = x, \quad x \in X. \quad (6)$$

The functions $\phi_t: X \rightarrow X$ defined for each $t \in T$ by $\phi_t(x) = \phi(t, x)$ form a set G , usually called a flow, with the following algebraic properties.

(1) $\phi_{t+s} = \phi_t \circ \phi_s = \phi_s \circ \phi_t$ (for $t, s, t+s \in T$) belongs also to the set G (where \circ indicates the composition of functions). If $T = [0, \infty)$, $t, s \in T$ implies that $t+s \in T$, and G is closed under its operation and is therefore a semigroup. G is commutative (Abelian).

(2) ϕ_0 is the identity function on X , i. e., $\phi_t = \phi_0 \circ \phi_t = \phi_t \circ \phi_0$. Then G has an identity element ϕ_0 and G is a commutative monoid. When $T = R$, and every ϕ_t is a diffeomorphism, we also have $\phi_t \circ \phi_{-t} = \phi_{-t} \circ \phi_t = \phi_0$.

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In such a case, G is a (commutative) group. We note that ϕ_{-t} is the inverse function of ϕ_t and the inverse element of ϕ_t in the group G .

Suppose we have the pdf of x_0 , $p_0(x)$. There exists a stochastic process $\{X_t, t \in T\}$, where $X_t(\omega) = \phi_t(X_0(\omega))$,¹⁴ i. e., the solution to Eq. (3) that has the value $x_0 = X_0(\omega)$ at $t=0$. Under these conditions, $\{X_t, t \in T\}$ is a diffusion process with drift velocity F and zero diffusion matrix. Since a diffusion process is a special case of a Markov process, we have the associated transition probabilities that permit us to define the semigroup of Markov transition operators. From the infinitesimal generator of this semigroup, Kolmogorov's backward and forward (Fokker-Planck) equations are obtained for the associated conditional transition densities. The density $p: T \times X \rightarrow R$, defined by $p(t, x) \equiv p_t(x)$, is governed by the Fokker-Planck equation,¹⁵ which in this case reduces to

$$\partial p / \partial t + \text{div}(Fp) = 0, \quad (7)$$

$$\begin{aligned} \dot{I}(t) &= \int_{S_0} \left\{ \left[\frac{\partial p}{\partial t}(t, \phi_t(x)) + \langle \text{grad } p(t, \phi_t(x)), \frac{\partial \phi}{\partial t}(t, x) \rangle \right] J(t, x) + p(t, \phi_t(x)) \frac{\partial J}{\partial t}(t, x) \right\} dx \\ &= \int_{S_0} \left[\frac{\partial p}{\partial t}(t, \phi_t(x)) + \langle \text{grad } p(t, \phi_t(x)), F(\phi(t, x)) \rangle + \frac{p(t, \phi_t(x))}{J(t, x)} \frac{\partial J}{\partial t}(t, x) \right] J(t, x) dx \\ &= \int_{S_t} \left[\frac{\partial p(t, y)}{\partial t} + \langle \text{grad } p(t, y), F(y) \rangle + p(t, y) \text{div } F(y) \right] dy = 0, \end{aligned} \quad (12)$$

where we have used Eq. (5) and the relations $\phi_t(x) = \phi_t \circ \phi_{-t}(y) = \phi_0(y) = y$ and

$$\frac{\partial J / \partial t(t, x)}{J(t, x)} = \text{div } F(\phi_t(x)),$$

and where $\langle A, B \rangle$ denotes the usual inner product in R^{n+m} . Since the domain of integration S_t is arbitrary, Eq. (7) is obtained from the vanishing of the integrand of Eq. (12).

Because the last m elements of F are zero, Eq. (7) can be written in the form

$$\frac{\partial p}{\partial t} + \sum_{i=1}^n \frac{\partial}{\partial x_i} (p f_i) = 0, \quad (13)$$

where the absence of derivatives in the k directions is noted. Equation (13) is the basis of our subsequent investigation.

The first-order sensitivity coefficients referred to in Sec. I can be expressed as

$$\beta_{ij}(t) = \frac{\partial \phi_i}{\partial x_j}(t, \phi(t, \bar{x}_0)), \quad (14)$$

$$i = 1, 2, \dots, n, \quad j = n+1, n+2, \dots, n+m.$$

As noted, these coefficients can be used to assess the effect of variations of the parameters in the trajectories of the system about \bar{k} . In the case considered here, it seems appropriate to define the *stochastic sensitivity coefficients*

$$q_j(t, x) = \frac{\partial p}{\partial k_j}(t, x), \quad j = 1, 2, \dots, m. \quad (15)$$

$$p(0, x) = p_0(x), \quad x \in X. \quad (8)$$

Equations (7) and (8) may be derived in a way that illustrates the nature of the problem we are considering. Since it is assumed that each ϕ_t is a diffeomorphism,

$$P_0(S_0) = P_t(\phi_t(S_0)) = P_t(S_t) = I(t), \quad (9)$$

where $P_t(S_t)$ is the probability that the system state lies in S_t . Equation (9) is equivalent to the statement of conservation of probability, also expressed by

$$\dot{I}(t) = \frac{d}{dt} \int_{S_t} P_t d\mu = \frac{d}{dt} \int_{S_t} p(t, y) dy = 0. \quad (10)$$

If we define the Jacobian $J(t, x) = \det(d\phi_t)(x)$, $x \in X$, we can make the change of variable $y = \phi_t(x) = \phi(t, x)$ and differentiate

$$I(t) = \int_{S_0} p(t, \phi(t, x)) J(t, x) dx, \quad (11)$$

to obtain

Evolution equations for the q_j can be derived directly from Eq. (13) as

$$\begin{aligned} \frac{\partial q_j}{\partial t} + \sum_{i=1}^n \left(\frac{\partial f_i}{\partial x_i} q_j + p \frac{\partial^2 f_i}{\partial x_i \partial k_j} + f_i \frac{\partial q_j}{\partial x_i} + \frac{\partial p}{\partial x_i} \frac{\partial f_i}{\partial k_j} \right) &= 0, \\ j = 1, 2, \dots, m. \end{aligned} \quad (16)$$

A global sensitivity measure is the expected value of $x_i(t)$, $m_i(t) = E\{x_i(t)\}$, which can be calculated from $p(t, x)$,

$$m_i(t) = \int_X x_i p(t, x) dx, \quad (17)$$

or by

$$m_i(t) = \int_{X_0} \phi_i(t, x) p_0(x_0) dx_0. \quad (18)$$

A simple evolution equation for m_i cannot be derived in general. Equations (7) and (8) can be used to provide associated equations for $\hat{p}(t, \xi)$ the Fourier transform of $p(t, x)$, the solution of which yields the expected value from

$$m_i(t) = (-1)(\partial \hat{p} / \partial \xi_i)_{t=0}. \quad (19)$$

III. SOLUTION OF EQ. (7)

Using the method of characteristics, the solution of Eqs. (7) and (8) can be expressed as

$$\begin{aligned} p(t, x) &= p_0(\phi(-t, x)) \\ &\times \exp \left[- \int_0^t \text{div } F[\phi(\tau, \phi(-t, x))] d\tau \right]. \end{aligned} \quad (20)$$

In the one-dimensional case ($n=1$), Eq. (20) reduces to

$$p(t, x) = p_0(x_0) \frac{f(x_0)}{f(x)}, \quad (21)$$

where $x_0 = \phi(-t, x)$.

Equation (20) can be interpreted in terms of the Jacobian of the system $J(t, x)$. For example, in one dimension, the factor $f(x_0)/f(x)$ is $1/J(t, \phi(-t, x))$, the Jacobian of the transformation ϕ_{-t} at x , which is the inverse of the Jacobian of ϕ_t at x_0 .¹⁶ In higher ($n > 1$) dimensions,

$$J(t, x) = C(x) \exp \int_0^t \operatorname{div} F(\phi(\tau, x)) d\tau. \quad (22)$$

To determine $C(x)$, we note that $J(0, x) = 1$, $x \in X$. Therefore, $C(x) = 1$. The second factor of Eq. (20) is obtained for $1/J(t, \phi(-t, x))$. The importance of the Jacobian formalism stems from the interpretation of

$$p(t, x) = p_0(x_0)/J(t, x_0). \quad (23)$$

Since the Jacobian is a measure of the local change of area in phase space due to the transformation ϕ_t , Eq. (23) indicates that, along system trajectories, p increases as long as ϕ_t is contracting and decreases if ϕ_t is expanding. This observation is intuitively consistent with the principle of conservation of probability Eq. (9). In the linear case $f(x) = Ax$, $\phi(t, x) = e^{At}x$, and $J(t, x) = \det e^{At}$. Thus, the eigenvalues of A determine the contracting or expanding character of the flow in each eigenspace of X . When all the eigenvalues of A have negative real parts, ϕ is a contraction that sends every trajectory to the sink $0 \in R^n$. When all eigenvalues of A have nonzero real parts of mixed signs, the system exhibits hyperbolic flows.

Some comments concerning the numerical solution of Eq. (13) can be made. Because of the absence of derivatives in the k direction, numerical schemes solved repeatedly along lines of different k values will be feasible. The simplest finite-difference approach to solving Eq. (13) is, in one dimension,

$$p(t + \Delta t, x) = p(t, x) - \left[p(t, x) \frac{\partial f}{\partial x}(x) + f(x) \frac{\Delta p}{\Delta x}(t, x) \right] \Delta t \quad (24)$$

for each value of k . If we use

$$p(t + \Delta t, x) = p(t, x) + \frac{\partial p}{\partial t} \Delta t + \frac{\partial^2 p}{\partial t^2} \frac{\Delta t^2}{2} + \dots, \quad (25)$$

terms of second and higher order in Δt can be retained through

$$\frac{\partial p}{\partial t} = -f \frac{\partial p}{\partial x} - p \frac{\partial f}{\partial x}, \quad (26)$$

$$\frac{\partial^2 p}{\partial t^2} = -\frac{\partial}{\partial x} \left(f \frac{\partial(f p)}{\partial x} \right), \quad (27)$$

so that the simplicity of the march in the t direction is maintained.

The associated equation for q Eq. (16) can be treated similarly to Eq. (13), marching to $t + \Delta t$ based on p and

q at t or solving first for $p(t + \Delta t, x)$ and then using these values and $q(t, x)$ to evaluate $q(t + \Delta t, x)$.

When x_0 is specified, the formalism of the Dirac delta function allows us to consider that problem as a special case of the general theory. For example, say that $f(z, k) = -kz^2$, $k > 0$, $z > 0$. The initial condition is specified at z_0 , i.e., $p_0(z) = \delta(z - z_0)$. The pdf of k is given as $p_1(k)$. Here, $X = Z \times K$, $Z = K = R_+$. Then it is easily verified that

$$\phi(t, z, k) = \frac{z}{1 + kzt}. \quad (28)$$

The Jacobian for this system is $J(t, x) = (1 + kzt)^{-2}$. The initial state is related to that at any time t by

$$z_0 = \phi(-t, z, k) = \frac{z}{1 - kzt}, \quad (29)$$

so $J(t, x_0) = (1 - kzt)^{-2}$. The joint pdf for z and k from Eq. (23) is therefore

$$p(t, z, k) = \frac{\delta[z/(1 - kzt) - z_0] p_1(k)}{(1 - kzt)^2}. \quad (30)$$

The interpretation of Eq. (30) relies on the following result from distribution theory.¹⁷ If U is a differentiable function with simple zeros u_1, u_2, \dots , then

$$\delta[U(z)] = \sum_i \frac{\delta(z - u_i)}{|U'(u_i)|}. \quad (31)$$

Letting $U(z) = [z/(1 - kzt)] - z_0$, we obtain

$$\delta\left(\frac{z}{1 - kzt} - z_0\right) = \frac{\delta[z - z_0/(1 + kz_0 t)]}{(1 + kz_0 t)^2}. \quad (32)$$

IV. SENSITIVITY ANALYSIS OF A REACTION MECHANISM FOR THE PHOTOLYSIS OF A MIXTURE OF CO, NO, NO₂, H₂O, AND AIR

A mechanism that exhibits many of the important features of atmospheric systems involving hydrocarbons and nitrogen oxides is that for the photolysis of a mixture of CO, NO, NO₂, and H₂O in air, given in Table I. We wish to explore the sensitivity of the concentrations of NO and NO₂ to uncertainty in the two photolysis rate constants k_1 and k_4 , and to uncertainty in the initial concentrations of NO and NO₂. Invoking the pseudo-steady-state approximation for the concentrations of O, O(¹D), OH, H, HO₂, and O₃, and letting $x = [\text{NO}_2]$, $y = [\text{NO}]$, $C = k_4 k_6 [\text{H}_2\text{O}] / (k_5 [M] + k_8 [\text{H}_2\text{O}])$, and $D = k_7 [\text{CO}] / k_{10}$, the system is described by

$$\frac{dx}{dt} = \frac{k_1 C(2D - 3x)}{k_3 y + C}, \quad (33)$$

$$\frac{dy}{dt} = \frac{k_4 C(x - 2D)}{k_3 y + C}. \quad (34)$$

(For notational simplicity we use x and y as the concentrations, rather than x_1 and x_2 .)

We note that for $y > 0$, the denominators of the right-hand sides of Eqs. (33) and (34) are nonzero. In the open half-plane ($y > 0$) of the phase space (x, y), existence and uniqueness of the trajectories are guaranteed. We have

TABLE I. Simplified reaction mechanism for the photolysis of a mixture of CO, NO, NO₂, and H₂O in air.

Reaction ^a	Rate constant at 298 K ^b
1. NO ₂ + hν → NO + O	0.51 min ⁻¹ °
2. O + O ₂ + M → O ₃ + M	2.08 × 10 ⁻⁵ ppm ⁻² min ⁻¹
3. NO + O ₃ → NO ₂ + O ₂	26.5 ppm ⁻¹ min ⁻¹
4. O ₃ + hν → O(¹ D) + O ₂	0.033 min ⁻¹ °
5. O(¹ D) + M → O + M	6.62 × 10 ⁴ ppm ⁻¹ min ⁻¹
6. O(¹ D) + H ₂ O → 2OH·	4.1 × 10 ⁵ ppm ⁻¹ min ⁻¹
7. CO + OH· → CO ₂ + H·	4.1 × 10 ² ppm ⁻¹ min ⁻¹
8. H· + O ₂ + M → HO ₂ · + M	instantaneous
9. HO ₂ · + NO → NO ₂ + OH·	1.2 × 10 ⁴ ppm ⁻¹ min ⁻¹
10. OH· + NO ₂ → HNO ₃	1.8 × 10 ⁴ ppm ⁻¹ min ⁻¹

^aThe reactions given, together with the two negligible reactions, O + H → OH and 2O → O₂ constitute a complete system *R* of reactions for the chemical species *S* involved, in the sense that any other reaction among members of *S* is a linear combination of equations in *R*. Minimal sets of nine equations, equivalent to *R*, can be derived from the usual atomic balances; but the rate constants are not always known.

^bReference 18.

[°]The values of *k*₁ and *k*₄ given are taken as the nominal values \bar{k}_1 and \bar{k}_4 . Sensitivity of the mechanism to their uncertainty is studied.

$$\frac{dy}{dx} = -\frac{2D-x}{2D-3x} \quad (35)$$

Equation (35) is equivalent to Eqs. (33) and (34) except for the line $x = x^* = 2D/3$, which is a trajectory of Eqs. (33) and (34).

The evolution of the (*x*, *y*) phase space trajectories from a region *ABCD* at *t* = 0 to the region *A'B'C'D'* at *t* ≈ 8 × 10⁴ min is shown in Fig. 1. As the trajectories approach $x^* = 2D/3$, the contracting nature of the flow is observed. The region *ABCD* can be assumed to represent the region of uncertainty in the initial values of *x* and *y*, the concentrations of NO₂ and NO. Probability density functions for *x*₀ and *y*₀, *p*₀(*x*, *y*), may be assigned on *ABCD*.

It is useful to divide the phase space into regions $x > x^*$ and $x < x^*$. The solution of Eq. (35) in the region $x > x^*$ is

$$y = Q - \frac{1}{3} \left[x - \frac{4D}{3} \ln(3x - 2D) \right], \quad (36)$$

where *Q* is a constant of integration. Using Eq. (33) we obtain an implicit solution for *x* as a function of time *t*,

$$k_3 [u - 2Dv(v-1)] + Rv = 27k_1 Ct + S, \quad (37)$$

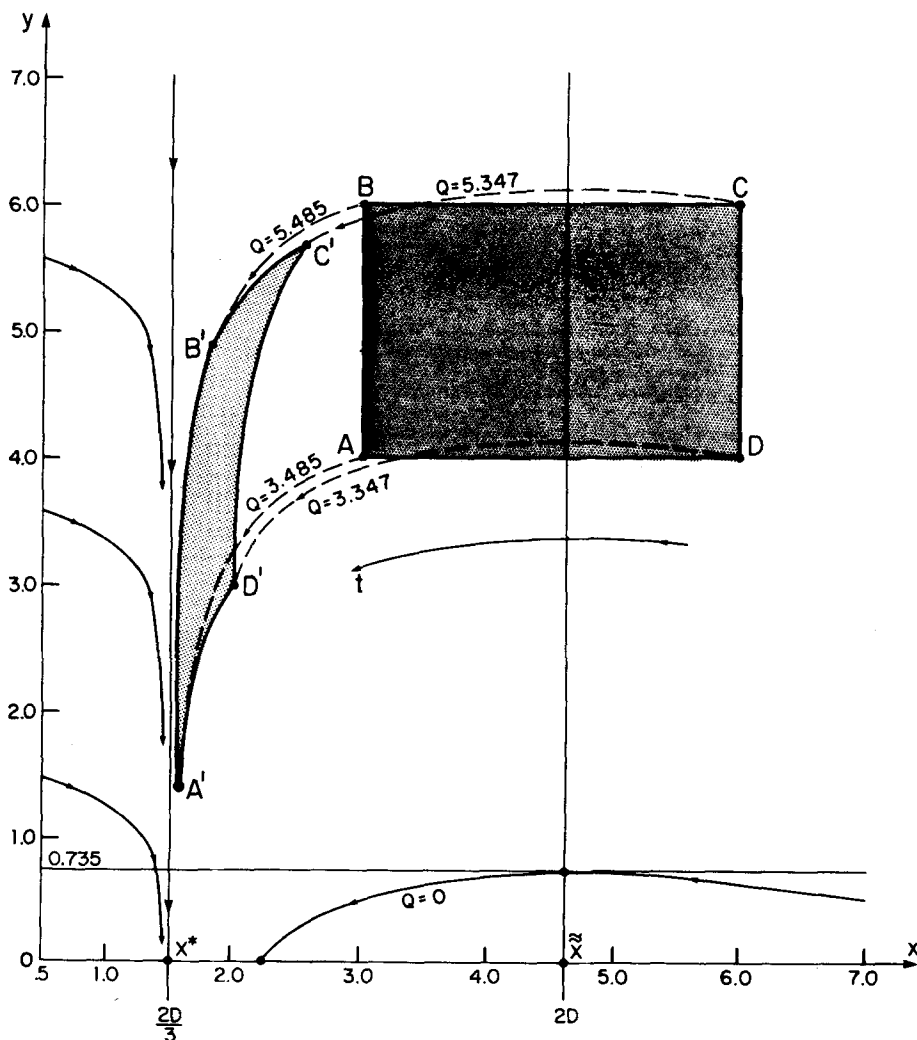


FIG. 1. Phase plane trajectories for *y* (the concentration of NO) and *x* (the concentration of NO₂) evolving from an initial condition region *ABCD*. Each point in *ABCD* evolves along a line of constant *Q*. The line $x^* = 2D/3$ is a singular trajectory of the system. The maximum value of *y* is achieved at $x = 2D$ for every trajectory.

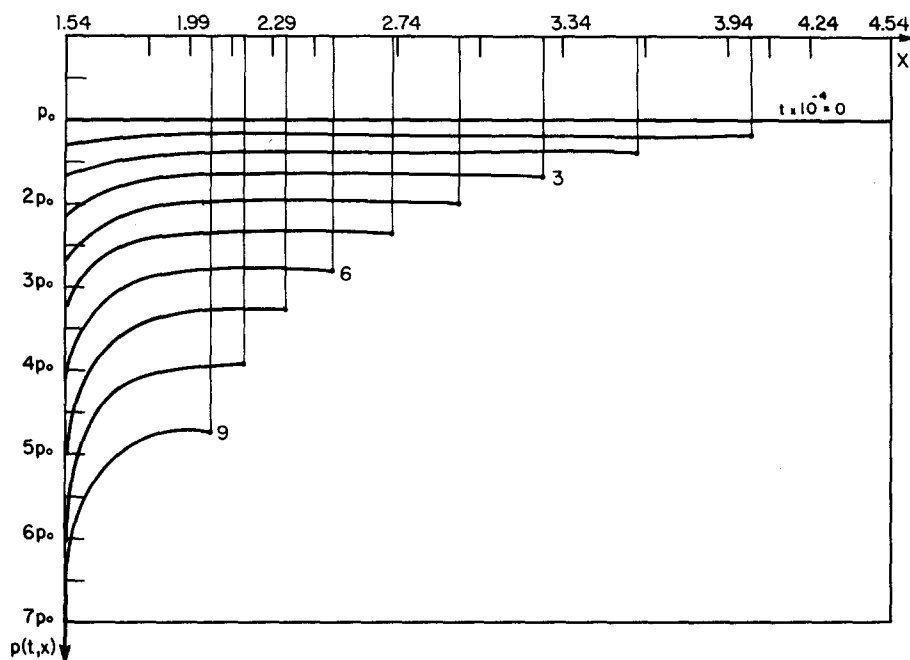


FIG. 2. Probability density function of the NO_2 concentration at times ranging from $t=0$ to $t=9 \times 10^4$ min along the trajectory $Q=5.485$ for the values of $k_1=\bar{k}_1=0.51$ and $k_4=\bar{k}_4=0.033$. The initial probability density of x was assumed to be uniform over $(1.54, 4.54)$.

where $u=3x-2D$, $v=\ln u$, $R=-9(C+k_3Q)$, and S is the second integration constant. Equation (37) can be simplified to

$$l^2 = \alpha - \beta e^l \quad (38)$$

by the transformations

$$l = v - \frac{1}{2} - \frac{R}{4Dk_3},$$

$$\alpha = \frac{(2Dk_3 + R)^2 - 8Dk_3(S + 27k_1 Ct)}{16D^2 k_3^2},$$

$$\beta = -\frac{1}{2D} \exp\left(\frac{1}{2} + \frac{R}{4Dk_3}\right).$$

The joint pdf for l , k_1 , and k_4 is then

$$p(t, l, k_1, k_4) = p_0(l_0, k_1, k_4) \frac{l^2 + \beta e^l}{l_0^2 + \beta e^{l_0}}. \quad (39)$$

The pdf p can also be determined by numerical solution of the appropriate form of Eq. (13). Denoting the right-hand sides of Eqs. (33) and (34) by $g(x, y)$ and $h(x, y)$, respectively, Eq. (13) becomes

$$\frac{\partial p}{\partial t} + g \frac{\partial p}{\partial x} + h \frac{\partial p}{\partial y} + p \left(\frac{\partial g}{\partial x} + \frac{\partial h}{\partial y} \right) = 0. \quad (40)$$

If we consider Q as a function of x and y ,

$$Q(x, y) = y + \frac{1}{3} \left[x - \frac{4D}{3} \ln(3x - 2D) \right], \quad (41)$$

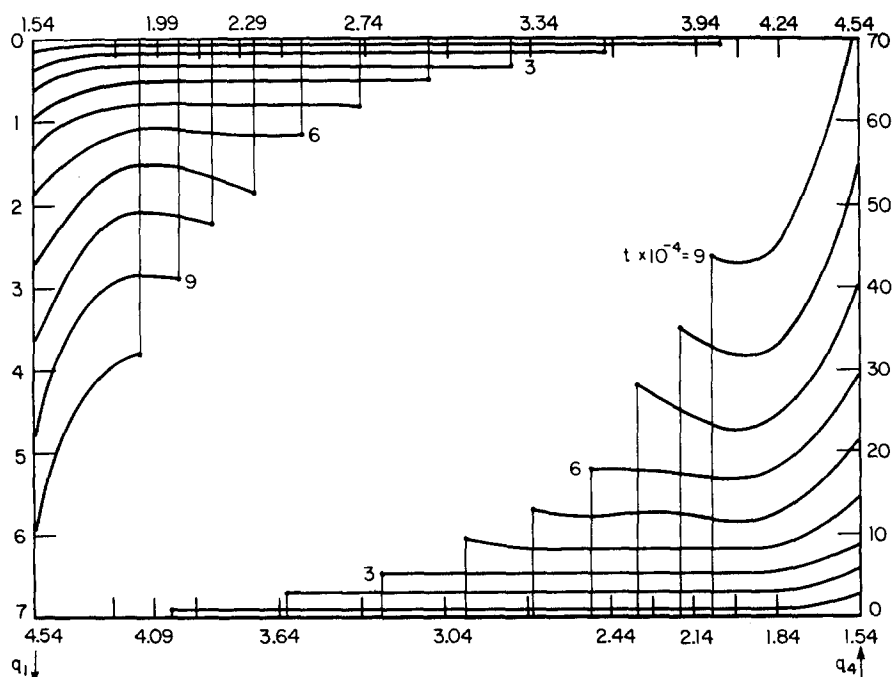


FIG. 3. The stochastic sensitivity coefficients $q_1 = \partial p / \partial k_1$, $q_4 = \partial p / \partial k_4$ at times ranging from $t=0$ to $t=9 \times 10^4$ min along the trajectory $Q=5.485$, evaluated for the values $k_1=\bar{k}_1=0.51$ and $k_4=\bar{k}_4=0.033$. The initial probability density was assumed to be uniform in some open set of $X \times K$, and equal to $p_0(x, y, k_1, k_4) = 0.2$.

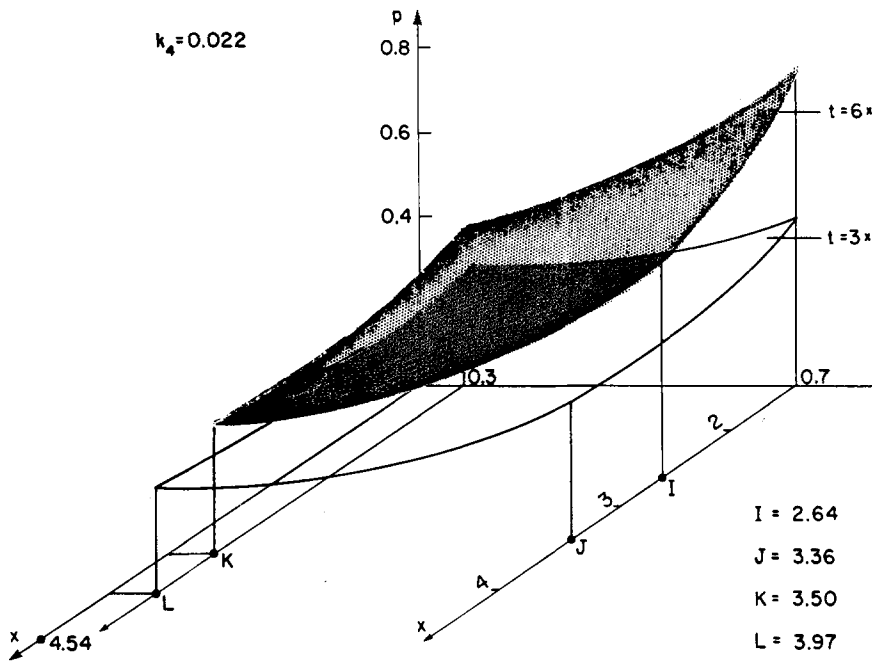


FIG. 4. Joint probability density function of the NO₂ concentration and k_1 at $t=3 \times 10^4$ and 6×10^4 min for $Q=5.485$ and $k_4=0.022$.

the transformation of coordinates $\lambda: (x, y) \rightarrow (x, Q(x, y))$ is a diffeomorphism leading to the equation

$$\frac{\partial \bar{p}}{\partial t} + \bar{g} \frac{\partial \bar{p}}{\partial x} + \bar{p} \left(\frac{\partial \bar{g}}{\partial x} + \frac{\partial \bar{h}}{\partial y} \right) = 0, \quad (42)$$

where

$$\bar{p} = p \circ \lambda^{-1}, \quad \bar{g} = g \circ \lambda^{-1},$$

and

$$\frac{\partial \bar{g}}{\partial x} = \frac{\partial g}{\partial x} \circ \lambda^{-1}.$$

Equation (42) does not contain a term involving $\partial \bar{p} / \partial Q$, which allows us to construct numerical schemes along lines of constant Q . With the same transformation, the equations for the stochastic sensitivity coefficients

$$q_1 = \partial p / \partial k_1, \quad q_4 = \partial p / \partial k_4, \quad (43)$$

lead to equations without Q derivatives,

$$\frac{\partial \bar{q}_i}{\partial t} + \frac{\partial \bar{g}}{\partial k_i} \frac{\partial \bar{p}}{\partial x} + \bar{g} \frac{\partial \bar{q}_i}{\partial x} + \bar{q}_i \left(\frac{\partial \bar{g}}{\partial x} + \frac{\partial \bar{h}}{\partial y} \right) + \bar{p} \left(\frac{\partial^2 \bar{g}}{\partial x \partial k_i} + \frac{\partial^2 \bar{h}}{\partial y \partial k_i} \right) = 0, \quad (44)$$

where the overbars should be interpreted as in Eq. (42).

The simplification arises, in this special case, from the fact that $h/g = (2D - x)/(3x - 2D)$ is independent of k_1 and k_4 .

Figure 2 shows the evolution of $p(t, x)$ along the trajectory with $Q=5.485$ for times ranging up to 9×10^4 for an initial uniform density. This figure shows only

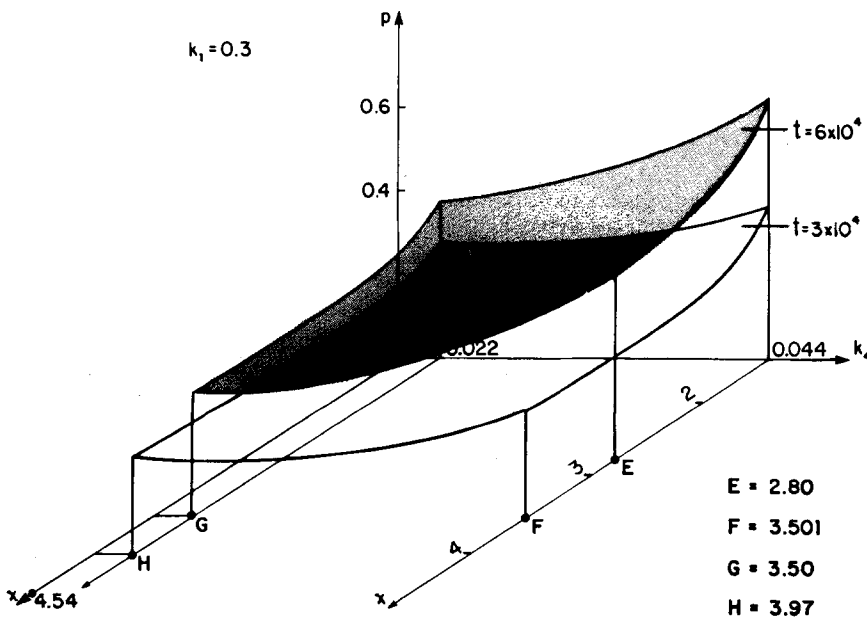


FIG. 5. Joint probability density function of the NO₂ concentration and k_4 at $t=3 \times 10^4$ and 6×10^4 min for $Q=5.485$ and $k_1=0.3$.

the evolution of the pdf resulting from uncertain initial conditions; at all times k_1 and k_4 are constant at their nominal values. The results in Fig. 2 were obtained using an explicit, first-order finite difference scheme. The numerical results, obtained for $\Delta t = 25$ and $\Delta x = 0.01$, were compared to the analytical solution Eq. (39) with good agreement.

The stochastic sensitivity coefficients q_1 and q_4 are shown in Fig. 3. An order of magnitude difference in the influence of the two parameters on \dot{p} for almost all values of x and t is seen. Changes in the parameter values affect the solutions most strongly near $x = x^*$.

Figure 4 shows $p(t, x)$ at $t = 3 \times 10^4$ and $t = 6 \times 10^4$ for $Q = 5.485$, $k_4 = 0.022$, and k_1 ranging over its domain. Likewise, Fig. 5 shows $p(t, x)$ at the same two times for $k_1 = 0.3$ and k_4 ranging over its domain. These two figures indicate how the system pdf depends on the parameter values. Physically, an increase in either of the constants k_1 or k_4 leads to an increase in the overall reactivity of the system and a higher probability density associated with values of x near x^* .

V. DISCUSSION AND CONCLUSIONS

The concept of stochastic sensitivity analysis has been developed as calculating the probability density function (pdf) of the concentrations of a set of species governed by

$$dx/dt = f(x; k), \quad x(0) = x_0,$$

given the pdf's of the parameter k and the initial conditions x_0 . The desired pdf, $p(x, t)$ was found to satisfy the equation

$$\partial p / \partial t + \text{div}(fp) = 0,$$

the solution of which has been discussed. The procedures suggested in Sec. III [Eqs. (24)–(27)] reveal that, for each value of k , an initial value problem similar to a vector ODE is to be solved. Thus the numerical effort needed to obtain the desired pdf's is comparable to that of the FAST method,^{10–12} as long as the same number of values in the parameter space K is used. The information obtained in the present method and in the FAST method is somewhat different. Whereas the FAST method yields the individual relative contribution of each parameter's uncertainty to the total uncertainty in each concentration as a function of time, the present method gives the joint pdf of all concentrations and parameters as a function of time. Expected values and higher moments can be determined from \dot{p} by integration.

The concept of a stochastic sensitivity coefficient $q_i = \partial p / \partial k_i$ was introduced. Evolution equations for the q_i were derived in general and solved in particular for the example studied.

- ¹Equation (1) is expressed in the autonomous form. If f is an explicit function of time t , the system can be converted to an $(n+1)$ -dimensional autonomous system by letting $dx_{n+1}/dt = 1$, with $x_{n+1}(0) = 0$.
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- ¹³Equations (5) and (6) can sometimes be guaranteed for $T = [0, \infty)$. In many cases T can be extended to R and X can be a differentiable manifold.
- ¹⁴ ω denotes the elementary event of the underlying probability space (Ω, F, P) . Each $X_t: \Omega \rightarrow X \subset R^n$, $t \in T$, induces a probability P_t on the Borel sets of R^n , defined by $P_t(B) = P(X_t^{-1}(B))$. The densities of the P_t are p_t . See, for example, L. Arnold, *Stochastic Differential Equations: Theory and Applications* (Wiley, New York, 1974).
- ¹⁵ X is not necessarily a Euclidean space, but a manifold that can be embedded in R^n for some n . In the example in Sec. IV, we choose to work in an open subset of R^2 . It is always possible to restrict probability densities defined on R^n to some regular subset X .
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