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Sensitivity Analysis of Ordinary Differential Equation Systems—A Direct Method*

ROBERT P. DICKINSON AND ROBERT J. GELINAS†

University of California, Lawrence Livermore Laboratory, Livermore, California 94550

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Given a system of time dependent ordinary differential equations, $\dot{y}_i = f_i(c_1, c_2, \ldots, y_1, y_2, \ldots, t)$, where c_k are rate parameters, we simultaneously solve for both y_i and a set of sensitivity functions, $\partial y_i/\partial c_k$, over all times t. These partial derivatives measure the sensitivity of the solution with respect to changes in the parameters c_k. Often these parameters are not accurately known. An example is given from atmospheric chemical kinetics using constant as well as time varying (diurnal) rate parameters. For the purposes of this paper, our calculations considered both first- and second-order contributions to Δy with respect to Δc. It is found that second-order sensitivity terms can be highly significant, but tend to be too costly for present widespread application.

I. INTRODUCTION

The need for systematic sensitivity analysis of large computational models is becoming increasingly apparent. This need is emerging as complex numerical models are increasingly applied for problem solving in numerious application areas that include atmospheric science, combustion physics and engineering (numerous types of applications), chemical laser studies, biological systems, and energy distribution and other socio–economic systems. Computational models can be based on algebraic equations, for static systems, and/or upon differential equations, for dynamic systems. Often, many of the parameters required for the solution of such systems are not known with great accuracy, nor are the parameter statistics always well known. The object of a sensitivity analysis is to systematically determine the effect of uncertain parameters on system solutions. This is useful in connection with both the sensitive and the insensitive factors in a system. For the former, one can measure the levels of effort and attention that may have to be devoted to various elements to which the system is sensitive. For the latter, it is

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† Present address: Science Applications Inc., P.O. Box 34, Pleasanton, California *94566*.

usually desirable to eliminate insensitive factors from model structures for computational reasons—provided it can be done with knowledgeable confidence.

This article can be viewed either independently or as a logical complement to an earlier article by Gelinas [1]. The earlier article emphasized approaches to solving potentially pathological sets of stiff ordinary, nonlinear, differential equations; the present article emphasizes the systematic determination of the sensitivity of those solutions to uncertainties in rate parameters and in initial conditions. While the subject of sensitivity analysis has been well known in control theory [2], there has been relatively little reduction to practice in the context of more general, large scale computational applications. (See also reference [3] for a good bibiliograph of work to date.) Two basic methods that have been applied are the Fourier amplitude sensitivity test (FAST) by Shuler, *et al.* [4, 5] and the direct method (DM) [2, 3], a version of which is presented here. Both the FAST and the DM approaches can yield higher-order sensitivity coefficients; but, to date, emphasis has been given primarialy to the linear portions of the theories. Both methods are presently at the dawn of large scale application and development, and certain elements of each method have yet to be completely understood and assimilated. Thus, advancing the state of general understanding and the state of specific application of sensitivity analysis methods for dynamic systems is our first priority. A detailed view of the computational implementation of the DM is also given, bringing out both the advantageous and the disadvantageous factors, as they are presently understood.

In Section II, the basic development for the DM algorithm is given. In Part A, the development of sensitivity equations is sketched. Consideration is given to a system of n differential equations with m parameters. For each parameter, n additional differential equations are developed which describe the sensitivity of the original system with respect to the chosen parameter. This second set of equations, which we call the sensitivity equations, will be solved simultaneously with the original system to yield linear sensitivity with respect to the chosen parameter.

Part B of Section II draws out what we call structural aspects of the actual implementation of the algorithm. We speak often in the context of chemical kinetics codes, which is where most of our work has been done. However, we believe these methods extend beyond this framework. This section discusses the Jacobian matrix and its significance in sensitivity analysis. Not only does the matrix directly enter into a description of the sensitivity equations, but its exact form will be needed in successfully solving certain difficult problems. This is in contrast to using numerical approximations of it while solving the differential equation systems.

Part C of Section II illustrates the evaluation of initial conditions for the variables of the sensitivity equations. These conditions vary slightly with respect to the type of parameter being studied.

Part D of Section II describes what we call the total linear sensitivity of the

differential equation system under study. A primary purpose of this paper is to convey to other potential users an algorithm for generating linear sensitivities z_i. It is possible in an analogous way to develop differential equations for quadratic sensitivities $\partial z_i/\partial c$. We have not done this because of the high computational cost for large problems and because the general problems associated with higher-order terms remain an open area for more effective research. However, if one does want to calculate quadratic terms, we show how our existing code can be simply modified to produce numerical estimates of these quantities. In fact for the purposes of the small example of Section III, we have performed this calculation and have provided an initial view of how quadratic sensitivities may affect the linear theory. For this purpose, Taylor's theorem is employed with remainder. As such, the error term involves the quadratic terms.

Section III will consider a simple example from atmospheric chemical kinetics. Various types of parameters will be discussed including time varying parameters which enter in consideration of diurnal problems.

Section IV describes and interprets numerical results for the selected example.

In other recent work, Atherton *et al.* [3] have employed a direct method for sensitivity analysis. It is significant to note that their work emphasizes statistical averages of sensitivity variables in contrast to the present work which considers the variables, per se. It is, of course, evident that approaches based on averaged sensitivities require statistical information on the distribution of sensitivity parameters, whereas the present approach does not. Both have merit, for a range of needs.

The work of Atherton, *et al.* also differs computationally from the present approach in a significant way. They solve the kinetics equations first, once and for all. This can be done since the kinetics differential equation system is independent of the sensitivity system. Using tabulated values of the kinetic system solutions and an interpolation scheme, the sensitivity equations may then be solved any number of times. This can be very efficient, but certain precautions are required. First, the interpolation approach requires considerable implementation effort beyond the basic existing kinetics program. Our method, on the other hand, can be readily implemented in such a program. Second, it is not presently known what effects interpolation errors may have on the accuracy and stability of the sensitivity calculations. Third, for large problems where the kinetic system is rapidly varying (e.g., diurnal or otherwise active systems) the mesh size necessary for sufficiently accurate interpolation could become prohibitively small, leading to potentially huge tabulations and storage demands. This would seem particularly true for diurnal problems in which solutions are obtained over very large time scales. Furthermore, we feel that the method adopted here could be used in a validation procedure to determine the suitability of the interpolation approach.

II. Basic Theory

A. *Development of Variational (Sensitivity) Equations*

Equations (1) below represent a time dependent system of nonlinear ordinary-differential equations (ODE) having solutions that are dependent upon certain rate parameters c, and initial conditions $y_i(0)$. That is,

$$\dot{y}_i = f_i(y_1, y_2, ..., y_n, t, c), \qquad i = 1, ..., n. \tag{1}$$

For notational convenience we shall rewrite the right-hand sides of (1) as $f_i(y, t, c)$, where y may be thought of as an n-vector (y_i). The solutions of (1) may be thought of as functions of two variables, t, c; that is, $y_i(c, t)$. The initial conditions, $y_i(0)$, will also be treated henceforth as parameters, c, in $y_i(c, t)$. A parameter is called sensitive if small changes in its value produce large changes in the solution to the problem. A reverse definition can be stated for a nonsensitive parameter.

We can next introduce n new variables (Z_i), which will numerically measure the sensitivity of the system (1) with respect to a parameter c.

$$Z_i = \partial y_i / \partial c, \qquad i = 1, ..., n. \tag{2}$$

The new variables will be found as the solutions to a new set of n differential equations, which we derive below. Actually, the system of differential equations for (Z_i) will be solved simultaneously with Eqs. (1) in the DM. The equations for (Z_i) are simply developed from two theorems of the calculus: the chain rule for differentiation, and the rule for interchanging the order of differentiation for certain mixed partials. We have

$$\dot{Z}_i = \frac{\partial}{\partial t}(Z_i) = \frac{\partial}{\partial t}\left(\frac{\partial y_i}{\partial c}\right) = \frac{\partial}{\partial c}\left(\frac{\partial y_i}{\partial t}\right),$$

or

$$\dot{Z}_i = \frac{\partial}{\partial c}(f_i(y(c, t), t, c)),$$

or

$$\dot{Z}_i = \frac{\partial f_i}{\partial c} + \sum_{j=1}^{n} \frac{\partial f_i}{\partial y_j} \frac{\partial y_j}{\partial c},$$

or finally

$$\dot{Z}_i = \frac{\partial f_i}{\partial c} + \sum_{j=1}^{n} \frac{\partial f_i}{\partial y_j} Z_j, \qquad i = 1, ..., n. \tag{3}$$

The term, $\partial f_i/\partial y_j$, of Eq. (3) is recognized to be an element of the Jacobian, J, of the original ODE system given by Eqs. (1); that is, J is an $n \times n$ matrix in which the (i,j) element $J_{i,j}$, is given by $\partial f_i/\partial y_j$. In vector notation Eqs. (3) are:

$$\dot{Z} = f_c + JZ = F^L, \tag{4}$$

where f_c is a vector of length n whose components are $\partial f_i/\partial c$, and the notation F^L is introduced for later use.

It should be noted that, if the parameter c does not appear explicitly in the f_i of (1), then (4) simplifies to $\dot{Z} = JZ$. This may be the case, for example, if the parameter c is an initial condition for one of the y_i.

B. *Structural Aspects of Solving Sensitivity Systems*

It is a straightforward matter to extend solution algorithms developed for Eqs. (1) such that the $2n$ equations of (1) and (4) may be solved simultaneously, in order to provide a sensitivity analysis. These implementations have, in fact, been done at LLL for our kinetics codes [6].

The extended kinetic-sensitivity system of $2n$ equations can be viewed as

$$\begin{bmatrix} \dot{X}_1 \\ \dot{X}_2 \\ \vdots \\ \dot{X}_n \\ \dot{X}_{n+1} \\ \vdots \\ \dot{X}_{2n} \end{bmatrix} = \begin{bmatrix} \dot{Y}_1 \\ \dot{Y}_2 \\ \vdots \\ \dot{Y}_n \\ \dot{Z}_1 \\ \dot{Z}_2 \\ \vdots \\ \dot{Z}_n \end{bmatrix} = \begin{bmatrix} F_1 \\ F_2 \\ \vdots \\ F_n \\ F_{n+1} \\ F_{n+2} \\ \vdots \\ F_{2n} \end{bmatrix} = \begin{bmatrix} F^U \\ F^L \end{bmatrix}, \tag{5}$$

where $F_1, F_2, \ldots, F_n$ are equal to $f_1, f_2, \ldots, f_n$, respectively, of Eqs. (1). These upper n elements of F will be denoted by F^U. We have introduced F_{n+1}, F_{2n}, which will be referred to as F^L to denote the right-hand sides of the equations for $\dot{Z}$, as given by Eq. (4) above.

Since the Jacobian is an important element of implicit ODE solution methods, it is well to examine the Jacobian structure of the extended system of $2n$ equations.

The Jacobian J_{2n}, for the $2n(y, Z)$ equations is defined by $\partial F/\partial X$ and has a particularly simple form:

$$J_{2n} = \left[\begin{array}{c|c} J & 0 \\ \hline A & J \end{array}\right]. \tag{6}$$

The two diagonal $(n \times n)$ blocks are just J, the Jacobian of the original system. The block of zeroes in the upper right corner reflects the fact that the original system of Eqs. (1) is decoupled from the Z_i. This fact, of course, yields a way of constructing a more efficient program for solution of the sensitivity problem. The solution of the expanded system depends on inversion of J_{2n}. Because of the special structure of J_{2n}, its inversion need only involve the inversion of J.

The jth column of the $(n \times n)$ matrix A in Eq. (6) is given by

$$A_j = (\partial f_c/\partial y_j) + (\partial J/\partial y_j)\, Z, \tag{7}$$

where we interpret $\partial f_c/\partial y_j$ to be an n vector whose ith component is $(\partial/\partial y_j)(\partial f_i/\partial c)$; i.e., the derivative of the ith component of f_c with respect to y_j. Similarly, we interpret $(\partial J/\partial y_j)$ as an $(n \times n)$ matrix whose (k, l) element is given by $\partial(J_{k,l})/\partial y_j$.

Since the individual parameters c, of the ODE system (1) are to be treated as being independent, it is possible to solve for the sensitivity, either one parameter at a time or for all parameters c, in a single calculation. This is a problem-dependent choice. Either way, the total number of equations to be solved is readily deduced. If there are m parameters $(c_1, c_2, \ldots, c_m)$ we could have mn new sensitivity equations to solve. When we add in the original system of n equations for $y(t)$. we arrive at a total of $(m + 1)\, n$ equations to solve.

Let us consider for a moment the Jacobian, $J_{(m+1)n}$, of the total (y, z) parametric system. The block structure of Eq. (8) is found convenient.

$$J_{(m+1)n} = \begin{bmatrix} J & 0 & 0 & & & \\ A_1 & J & 0 & & & \\ A_2 & 0 & J & & & \\ A_3 & 0 & 0 & J & & \\ \vdots & & & & \ddots & \\ & & & & & J \\ A_m & & & & & \end{bmatrix} \tag{8}$$

The matrix, block-wise, has as its only nonzero entries the first column and the diagonal. As before, the inversion of this matrix only requires the inversion of J, an $(n \times n)$ matrix. Now for the αth parameter c_α, of the set $(c_1, c_2, \ldots, c_m)$ we can write for the jth column of A_α

$$A_{\alpha_j} = (\partial f_{c_\alpha}/\partial y_j) + ((\partial/\partial y_j)\, J)\, Z_\alpha, \qquad \alpha = 1, \ldots, m, \tag{9}$$

where Z_α is the n vector whose kth component is $\partial y_k/\partial c_\alpha$. Notice that $((\partial/\partial y_j)\, J)$ does not change with α.

C. *Initial Conditions for the Sensitivity Variables* Z_i

Let us determine the initial conditions for the variational quantities, Z_i. The quantities $Z_i(0)$ are determined by the following limits:

$$Z_i(0) = \lim_{\Delta c \to 0} \frac{y_i(c + \Delta c, 0) - y_i(c, 0)}{\Delta c}. \tag{10}$$

Two cases now arise:

Case 1. The parameter c is not an initial condition of one of the y_i : clearly, $y_i(c + \Delta c, 0) - y_i(c, 0) = 0$ if c is not an initial condition. Thus, $Z_i(0) = 0$ for all i.

Case 2. The parameter c is an initial condition for, say, y_k. In this case $Z_i(0) = 0$ for $i \neq k$ for the same reasons mentioned above. But, for $i = k$, $y_k(c + \Delta c, 0) - y_k(c, 0) = \Delta c$, and the limit of Eq. (10) is 1. Thus, if c is an initial condition for y_k, $Z_i(0) = 0$ if $i \neq k$ and $Z_k(0) = 1$.

D. *Total Sensitivity*

We have seen that, for any particular c_k, n new variables $Z_1, \ldots, Z_n$, were defined that measure the sensitivity relative to c_k. Let us rename these quantities $Z_{i,k}$. We have also seen (in Section B) that, for independent parameters $c_1, c_2, \ldots, c_k, \ldots, c_m$, the quantities $Z_{i,k}$ can be solved simultaneously (an $(m + 1)n$ by $(m + 1)n$ system) or separately (a $2n \times 2n$ system, m times). Separate solution has the advantage of less computer storage and less logical complexity.

Having obtained the solutions for $Z_{i,k}$, a measure of the total variation, or total sensitivity, of y_i is given by evaluating[1]

$$\Delta y_i = \sum_{k=1}^{m} Z_{i,k} \Delta c_k + O((\max \Delta c_k)^2), \qquad i = 1, \ldots, n. \tag{11}$$

The possible importance of the higher-order terms has often been acknowledged, but a quantitative examination of such terms does not seem to have been made in specific applications. We now give a method for calculating and interpreting second-order derivatives, by simple modifications to our basic sensitivity code. This is done for the purpose of estimating the total error in the linear theory. In a later example, we give a numerical illustration of this procedure.

[1] One could evaluate the expectation values of Δy_i, or their variances. At least two basic factors presently recommended the direct consideration of the Δy_i in chemical kinetics: The statistical properties governing c are largely unavailable for important reaction rates. Second, the physical modeler is often most concerned with the extreme values that individual y_i components may assume as new parametric data is incorporated. It is well known that the averaging of Δy_i or of $(\Delta y_i)^2$, may suppress the extreme components.

These modifications can be explained best by simply considering a function $y(c, d, t)$ of two parameters, c and d, and time t. We use Taylor's theorem with remainder (see [7], with $n = 1$) and assume an expansion about the point (c_1, d_1) with t fixed. Letting $\Delta c = c_2 - c_1$, and letting $\Delta d = d_2 - d_1$ gives

$$\Delta y = \frac{\partial y}{\partial c}\Delta c + \frac{\partial y}{\partial d}\Delta d + Q, \tag{12}$$

where

$$Q = \frac{1}{2}\frac{\partial^2 y}{\partial c^2}(\Delta c)^2 + \frac{\partial^2 y}{\partial c\,\partial d}(\Delta c)(\Delta d) + \frac{1}{2}\frac{\partial^2 y}{\partial d^2}(\Delta d)^2. \tag{13}$$

The first partials will be evaluated at (c_1, d_1), but the second partials are evaluated at $(c_1 + \beta\,\Delta c, d_1 + \beta\,\Delta d)$, where $0 < \beta < 1$. Recall that, if the second partials are evaluated at the correct point on the line segment between the points (c_1, d_1, t) and (c_2, d_2, t), the expression Q in Eqs. (12) and (13), above, represents the total error in the linear theory.

In Eq. (12) the terms involving first derivatives are denoted by L (for linear). The second part is denoted by Q (for quadratic). For purposes of calculation, β is unknown; what we have done is to generate numerically a first-order approximation to the second-order partial derivatives evaluated at (c_1, d_1), that is at $\beta = 0$. Note that we are identifying Q with the total remainder, or error term, in the Taylor series, even though we are only estimating this quantity.

For example, $\partial^2 y/\partial c\partial d$ is evaluated in three steps. First, run the code calculating $\partial y/\partial d$ evaluated at the point $c = c_1$. Second, run the code calculating $\partial y/\partial d$ evaluated at the point $c = c_1 + \Delta c$. For these two runs store the partials on disk or tape. Third, form the numerical approximation to the desired second derivative by:

$$\frac{(\partial y/\partial d)|_{c_1+\Delta c} - (\partial y/\partial d)|_{c_1}}{\Delta c}.$$

The work involved for this type of calculation is tedious. For a system of n equations with m parameters one wishes to calculate $\partial^2 yk/\partial c_i\,\partial c_j$, where $k = 1,\ldots, n$ and $i, j = 1,\ldots, m$.

From calculus,

$$\partial^2 y_k/\partial c_i\,\partial c_j = \partial^2 y_k/\partial c_j\,\partial c_i, \tag{14}$$

which cuts the work down by almost one half. The number of partials to be calculated is then $m(m + 1)/2$ for each of the n species; and two runs must be made for each partial.

In what follows, notions are introduced, which should be useful to the user in the interpretation of graphical, as well as written, output. We relate relative

and absolute errors in y to similar errors in the parameters c. This analysis includes the quadratic error terms. Instead of considering y, let us now consider the relative change $\Delta y/y$, corresponding to a relative parameter change $\Delta c/c$. Of course, if the value of c is zero, then only absolute changes can be considered. As will be seen later, this is the case, for example, in considering the time varying parameters, where one evaluates $\partial y/\partial \epsilon$ at $\epsilon = 0$. In the discussion which follows, all parameters are constant and nonzero at their expansion point, and the Taylor formula is rewritten as

$$\begin{aligned} \frac{\Delta y}{y} &= \frac{1}{y}(L + Q) \\ &= \left(\frac{1}{y}\frac{\partial y}{\partial c}c\right)\frac{\Delta c}{c} + \left(\frac{1}{y}\frac{\partial y}{\partial d}d\right)\frac{\Delta d}{d} + \frac{1}{y}Q. \end{aligned} \tag{15}$$

For ease of explanation, let the coefficients of the linear part be called $a_1, a_2, \ldots$, and let the coefficients of the Q part be called $b_1, b_2, \ldots$. In this notation:

$$\frac{\Delta y}{y} = a_1\frac{\Delta c}{c} + a_2\frac{\Delta d}{d} + b_1\left(\frac{\Delta c}{c}\right)^2 + b_2\left(\frac{\Delta c}{c}\right)\left(\frac{\Delta d}{d}\right) + b_3\left(\frac{\Delta d}{d}\right)^2. \tag{16}$$

The output of the sensitivity code then records $a_1, a_2, \ldots$, as well as $\partial y/\partial c$ and $\partial y/\partial d \cdots$. Special procedures are necessary to calculate $b_1, b_2, \cdots$. Now let $L_{\text{rel}} = (1/y)\,L$ and let $Q_{\text{rel}} = (1/y)\,Q$. Thus,

$$\Delta y/y = L_{\text{rel}} + Q_{\text{rel}}. \tag{17}$$

Taking absolute values and using the triangle inequality ($|x + y| \leqslant |x| + |y|$) one has:

$$|\Delta y/y| \leqslant |L_{\text{rel}}| + |Q_{\text{rel}}| \leqslant |L|_{\text{rel}} + |Q|_{\text{rel}} \tag{18}$$

where

$$|L|_{\text{rel}} = |a_1|\,|\Delta c/c| + |a_2|\,|\Delta d/d| \tag{19}$$

and

$$|Q|_{\text{rel}} = |b_1|\,|\Delta c/c|^2 + |b_2|\,|\Delta c/c|\,|\Delta d/d| + |b_3|\,|\Delta d/d|^2. \tag{20}$$

It is natural to say that the theory, or sensitivity, at a point t is linear provided that $|L|_{\text{rel}}$ is much larger than $|Q|_{\text{rel}}$; and we indeed adopt this point of view.

The scaling conveniences associated with evaluations at $|\Delta c/c| = 1$ and $|\Delta d/d| = 1$ are evident both with respect to $|L|_{\text{rel}}$ and $|Q|_{\text{rel}}$ and with respect

to the individual terms in (19) and (20) involving $|a_i|$ and $|b_i|$. Thus, in later graphs we will consider (for $|\Delta c/c| = 1$ and $|\Delta d/d| = 1$)

$$|L|_{\text{total}} = \sum_i |a_i| \tag{21}$$

and

$$|Q|_{\text{total}} = \sum_i |b_i|, \tag{22}$$

as well as the individual terms $|a_i|$ and $|b_i|$, keeping in mind the linear and quadratic scaling properties, respectively, about this specific choice of evaluation points.

III. A Set of Examples

In this section, we present a compact example to illustrate three types of parametric sensitivities: (1) $\partial y_i/\partial c_k$, where c_k refers to initial conditions of either time varying or constant y_i's; (2) $\partial y_i/\partial c_k$, where c_k refers to constant rate coefficients; and (3) $\partial y_i/\partial c_k$, where c_k refers to time varying rate coefficients.

The example we have chosen is known as the Chapman mechanism for atmospheric ozone kinetics. It is composed of four reactions:

$$\mathrm{O} + \mathrm{O_2} \xrightarrow{M} \mathrm{O_3}: \qquad k_1 = 1.63E - 16$$

$$\mathrm{O} + \mathrm{O_3} \rightarrow 2\mathrm{O_2}: \qquad k_2 = 4.66E - 16$$

$$\mathrm{O_2} \xrightarrow{h\nu} 2\mathrm{O}: \qquad k_3 = 5.\ E - 11 \text{ (daily averaged solar flux)}$$

$$\mathrm{O_3} \xrightarrow{h\nu} \mathrm{O} + \mathrm{O_2}: \qquad k_4 = 2.5\ E - 4 \text{ (daily averaged solar flux)}$$

where k_1, k_2, k_3, and k_4 are reaction rate coefficients. We will consider cases in which k_3 and k_4 are constant as well as cases where they are time varying, as in diurnal systems.

The species concentrations ($\mathrm{cm^{-3}}$) are designated as

$$y_1(t) \equiv [\mathrm{O}],$$

$$y_2(t) \equiv [\mathrm{O_3}],$$

$$y_3(t) \equiv [\mathrm{O_2}],$$

We hold $[\mathrm{O_2}]$ constant and therefore have two differential equations:

$$\dot{y}_1(t) = f_1(y_1, y_2, y_3, k_1, k_2, k_3, k_4, t), \tag{23}$$

$$\dot{y}_2(t) = f_2(y_1, y_2, y_3, k_1, k_2, k_4, t), \tag{24}$$

where (suppressing some arguments)

$$f_1 \equiv 2k_3y_3 + k_4y_2 - k_1y_3y_1 - k_2y_1y_2 = F_1\,, \tag{25}$$

$$f_2 \equiv k_1y_3y_1 - k_2y_1y_2 - k_4y_2 = F_2\,. \tag{26}$$

$$y_1(0) = 1.E + 6, \tag{27}$$

$$y_2(0) = 1.E + 12, \tag{28}$$

$$y_3(0) = 3.7E + 16. \tag{29}$$

A common quantity to the three sensitivity types to be considered is the Jacobian J:

$$J = \begin{bmatrix} \partial f_1/\partial y_1 & \partial f_1/\partial y_2 \\ \partial f_2/\partial y_1 & \partial f_2/\partial y_2 \end{bmatrix}, \tag{30}$$

or

$$J = \begin{bmatrix} (-k_1y_3 - k_2y_2) & (k_4 - k_2y_1) \\ (k_1y_3 - k_2y_2) & (-k_2y_1 - k_4) \end{bmatrix}. \tag{31}$$

Type 1. *Sensitivity to Initial Conditions*

A. *Parameter c is an Initial Value for Time Varying Species*

Let the initial condition $y_1(o)$ have the value c. In this case c does not appear explicitly in f_1 or f_2, and f_c (see Eq. (4)) is therefore the zero vector. Thus we have:

$$\dot{Z} = JZ \tag{32}$$

with

$$Z_1(0) = 1, \tag{33}$$

$$Z_2(0) = 0. \tag{34}$$

If $c = y_2(0)$, we would have

$$Z_1(0) = 0, \tag{35}$$

$$Z_2(0) = 1. \tag{36}$$

To consider the Jacobian, J_{2n}, recall Eqs. (5)–(9). For the expanded system F_3 and F_4 of Eq. (5) are

$$F_3 = -(k_1y_3 + k_2y_2)\,Z_1 + (k_4 - k_2y_1)\,Z_2 \tag{37}$$

$$F_4 = (k_1y_3 - k_2y_2)\,Z_1 - (k_2y_1 - k_4)\,Z_2\,. \tag{38}$$

The matrix A in the lower left corner of J_{2n} is

$$A = \begin{bmatrix} \partial F_3/\partial y_1 & \partial F_3/\partial y_2 \\ \partial F_4/\partial y_1 & \partial F_4/\partial y_2 \end{bmatrix} = \begin{bmatrix} (-k_2 Z_2) & (-k_2 Z_1) \\ (-k_2 Z_2) & (-k_2 Z_1) \end{bmatrix}. \tag{39}$$

B. *Parameter c is an Initial Condition for Constant Species*

Let $c = y_3$. In this case c appears explicitly in f_1 and f_2. Thus we have

$$\dot{Z} = f_c + JZ = F^L, \tag{40}$$

with

$$Z_1(0) = Z_2(0) = 0, \tag{41}$$

and $f_c = \{(f_c)_i\}$, $i = 1, 2$, a vector of length two. In the present case

$$(f_c)_i \equiv \partial f_i/\partial c = \partial f_i/\partial y_3 ,$$

and

$$(f_c)_1 = 2k_3 - k_1 y_1 \tag{42}$$

$$(f_c)_2 = k_1 y_1 . \tag{43}$$

Again using Eq. (5)

$$F_3 = -(k_1 y_3 + k_2 y_2) Z_1 + (k_4 - k_2 y_1) Z_2 + (2k_3 - k_1 y_1), \tag{44}$$

and

$$F_4 = (k_1 y_3 - k_2 y_2) Z_1 - (k_2 y_1 + k_4) Z_2 + k_1 y_1 . \tag{45}$$

In this case we have

$$A = \begin{bmatrix} -(k_2 Z_2 + k_1) & (-k_2 Z_1) \\ -(k_2 Z_2 - k_1) & (-k_2 Z_1) \end{bmatrix}. \tag{46}$$

Type 2. Sensitivity to Constant Rate Coefficients

Using Eq. (4) for $c = k_l$, $l = 1,..., 4$, we have the sensitivity equations

$$\dot{Z} = f_{k_l} + JZ, \qquad l = 1,..., 4, \tag{47}$$

where

$$\dot{Z}_1 = (\partial f_1/\partial k_l) + (JZ)_1 , \qquad l = 1,..., 4, \tag{48}$$

and

$$\dot{Z}_2 = (\partial f_2/\partial k_l) + (JZ)_2 , \qquad l = 1,..., 4. \tag{49}$$

The initial conditions on Z are

$$Z_1(0) = Z_2(0) = 0. \tag{50}$$

To give an example of the structure of the matrix A in the lower left hand corner of J_{2n}, we will let $c = k_4$:

$$A = \begin{bmatrix} (-k_2 Z_2) & -(k_2 Z_1 - 1) \\ (-k_2 Z_2) & -(k_2 Z_1 + 1) \end{bmatrix}. \tag{51}$$

Type 3. *Sensitivity to Time Varying Rate Coefficients*

An important problem in atmospheric kinetics is to include diurnal time variations in the photodissociation rates k_3 and k_4. This is analogous to Type 2, above. In the present case, introducing $Z = (\partial/\partial\epsilon) y(k_l(t) + \epsilon g_l(t), y_1, y_2, \ldots, y_n, t)|_{\epsilon=0}$ we have

$$\dot{Z} = f_{k_l(t)} + JZ, \qquad l = 3, 4, \tag{52}$$

with

$$Z_1(0) = Z_2(0) = 0. \tag{53}$$

The functional derivative $f_{k_l(t)}$ can be evaluated as in variational calculus by introducing the quantity $\epsilon g_l(t)$, where ϵ is a real number and $g_l(t)$ is a function of t that measures the uncertainty in $k_l(t)$.

$$f_{k_l(t)} = (\partial/\partial\epsilon) f(k_l(t) + \epsilon g_l(t), y_1, y_2, \ldots, y_n, t)|_{\epsilon=0}. \tag{54}$$

It follows from (54), (25), and (26) that

$$f_{k_3(t)} = \begin{pmatrix} 2g_3(t)\, y_3 \\ 0 \end{pmatrix}, \tag{55}$$

$$f_{k_4(t)} = \begin{pmatrix} g_4(t)\, y_2 \\ -g_4(t)\, y_2 \end{pmatrix}. \tag{56}$$

Letting $c = k_4(t)$, the structure of the matrix A in J_{2n} is

$$A = \begin{bmatrix} (-k_2 Z_2) & -(k_2 Z_1 - g_4(t)) \\ (-k_2 Z_2) & -(k_2 Z_1 + g_4(t)) \end{bmatrix}. \tag{57}$$

For diurnal applications, a useful (but not exact) representation of $k_l(t)$ for $l = 3, 4$ is

$$k_l(t) = \exp -[\Sigma_l/\sin wt], \qquad \text{for} \quad \sin wt > 0, \quad l = 3, 4 \tag{58}$$

$$k_l(t) = 0, \qquad \text{for} \quad \sin wt \leqslant 0, \quad l = 3, 4. \tag{59}$$

We have defined

$$w \equiv 2\pi \left(\frac{1}{86400 \text{ sec/day}}\right) \tag{60}$$

$$\Sigma_l \equiv -\ln k_l(\text{noon}). \tag{61}$$

The examples below employ the numerical values $k_3(\text{noon}) = 1.5\,E\text{–}10$ and $k_4(\text{noon}) = 5.E\text{–}4$ which can be taken crudely to typify physical conditions at an altitude of approximately 35 km at 45° N latitude at the time of autumn equinox. One may take $g_l(t)$ to be

$$\frac{\partial k_l(t,\, k_l(\text{noon}))}{\partial k_l(\text{noon})}.$$

Thus, for our example

$$g_l(t) = (k_l(t)/k_l(\text{noon}))/\sin(wt), \qquad l = 3, 4. \tag{62}$$

With these choices one should observe that the change in y due to uncertainty in $k_l(\text{noon})$ is given by $\Delta y(t) = Z(t) * \Delta k_l(\text{noon})$.

With the information above, we have found it to be essentially the same task to solve the sensitivity system for $(y(t), Z(t))$, in fully automated fashion, as it was to solve just the chemical kinetic system for $(y(t))$. The results of such calculations are presented in the next section.

IV. Results

The time evolution of the concentrations [O] and $[O_3]$ are shown in Figs. 1 and 2, respectively, for two different types of calculation. The constant photodissociation rates used for k_3 and k_4 in the "constant rates" calculation are the appropriate daily averaged rates corresponding to the time varying diurnal photodissociation rates $k_3(t)$ and $k_4(t)$ (see Eqs. (60)–(64) used in the "diurnal rates" calculation. It

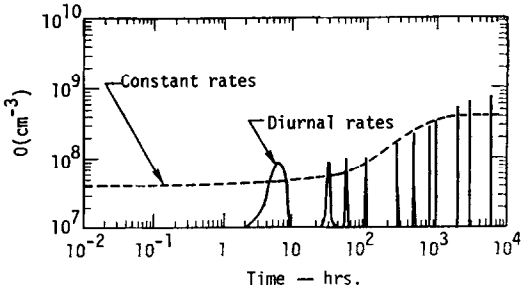

FIG. 1. Time evolution of O(cm^{-3}) for constant (daily averaged) rates and for diurnal rates.

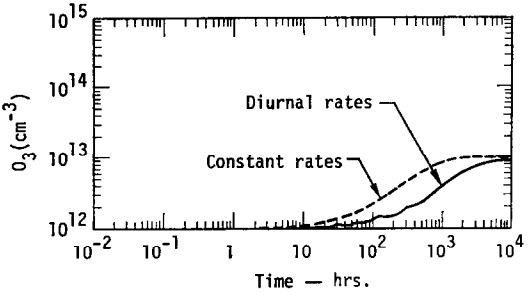

FIG. 2. Time evolution of $O_3(cm^{-3})$ for constant (daily averaged) rates and for diurnal rates.

is seen that $[O_3]$ does not respond instantaneously to solar flux variations and that the daily averaged photodissociation rates eventually yield the same *asymptotic* solutions for $[O_3]$ as in the more general diurnal calculations. Prior to asymptotic times significant discrepancies occur in $[O_3]$ due to the distinctly different kinetic sensitivities of the constant versus diurnal rate mechanisms. For the same reason discrepancies occur at all times for [0], since it responds instantaneously to solar flux variations throughout the problem history. In such cases there appears to be little, or no, mechanistic relevance associated with replacing instantaneous photodissociation rates by constant rates. These points tend to be important because of the widespread use of constant radiative rates in atmospheric applications. The remainder of this article presents detailed sensitivity results in support of these observations.

The sensitivities associated with the constant rate calculations are presented in Figs. 3–8. In Figs. 3 and 4 are shown plots of $| L |_{\text{total}}$ and $| Q |_{\text{total}}$ (of Eqs. (21)

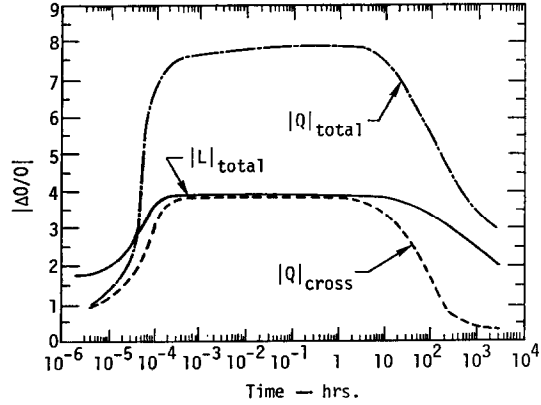

FIG. 3. Linear and quadratic sensitivities for $| \Delta O/O |$ with all $| \Delta c/c | = 1$ in constant rate calculations.

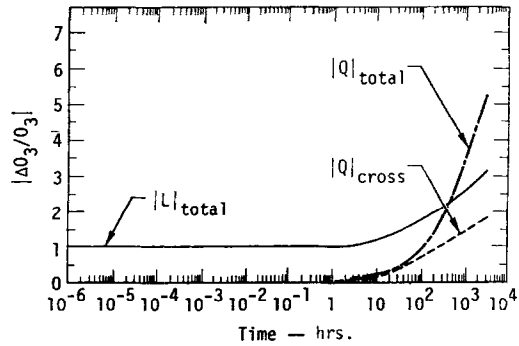

FIG. 4. Linear and quadratic sensitivities for $|\Delta O_3/O_3|$ with all $|\Delta c/c| = 1$ in constant rate calculations.

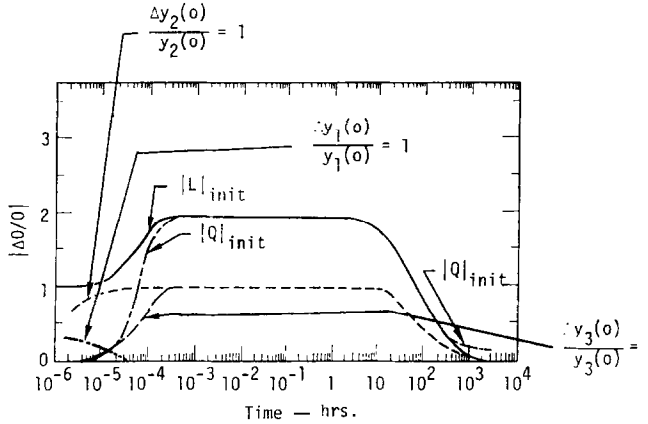

FIG. 5. Linear and quadratic initial condition sensitivity terms for $|\Delta O/O|$ in constant rate calculations.

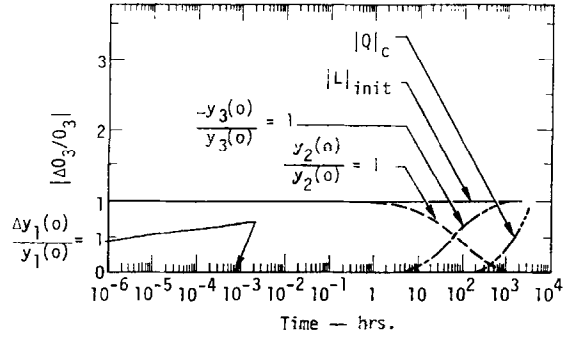

FIG. 6. Linear and quadratic initial condition sensitivity terms for $|\Delta O_3/O_3|$ in constant rate calculations.

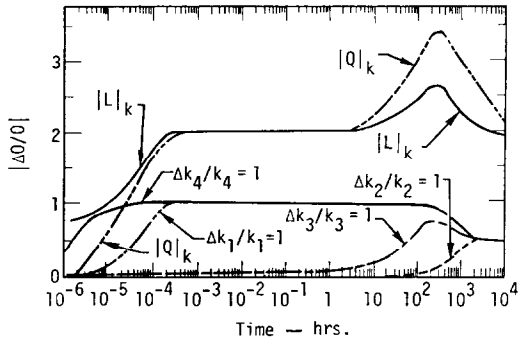

FIG. 7. Linear and quadratic rate sensitivity terms for | $\Delta O/O$ | in constant rate calculations.

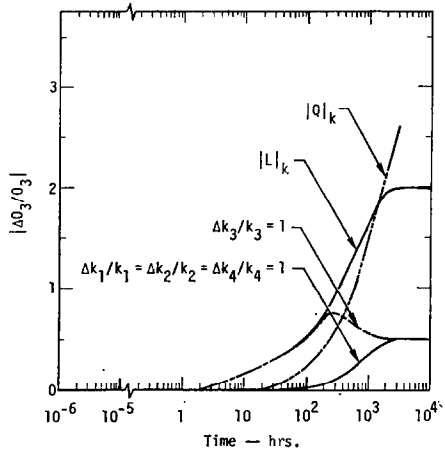

FIG. 8. Linear and quadratic rate sensitivity terms for | $\Delta O_3/O_3$ | in constant rate calculations.

and (22)) as well as a term called | Q |$_{\text{cross}}$. The data for | Q |$_{\text{cross}}$ consists only of the second-order "cross terms" in | Q |$_{\text{total}}$ that are dependent on two different parameters. It is evident that the second-order terms are significant at nearly all times for the sensitivity of [O] with the | $\Delta c/c$ |'s equal to unity, whereas it takes nearly a thousand hours for this to be true in the case of [O_3]. However, it is important to recall the scaling of the quadratic terms relative to the linear terms for any other values of $\Delta c/c$. For example, if | $\Delta c/c$ | = 0.1 for all parameters, the quadratic sensitivity drops to 0.01 | Q |$_{\text{total}}$, while the linear sensitivity only drops to 0.1 | L |$_{\text{total}}$. In the other extreme, if | $\Delta c/c$ | = 10, the quadratic sensitivity is 100 | Q |$_{\text{total}}$, while the linear sensitivity is 10 | L |$_{\text{total}}$. From this point of view, if | $\Delta c/c$ | is larger than 1, then it is all the more important that the user have a knowledge of the error Q in order to validate his linear results. Also recall

that the choice of viewing the absolute magnitudes of the sensitivities simply gives a worst case analysis. Nevertheless, the first quantitative look at second-order sensitivity terms tends to confirm earlier intuitions concerning the possible importance of higher-order sensitivity terms in physically interesting time regimes and uncertainty ranges.

Figures 5–8 are based on a further breakdown of $| L |_{\text{total}}$ and $| Q |_{\text{total}}$. Namely, $| L |_{\text{total}}$ is composed of two types of terms. One is the sum $| L |_{\text{init}} = \sum | a_i |$, where the sum is taken over terms only involving initial conditions. The other is a sum $| L |_k = \sum | a_i |$, where the terms only involve rate coefficients.

The further breakdown of $| Q |_{\text{total}}$ can be written

$$| Q |_{\text{total}} = | Q |_{\text{init}} + | Q |_k + | Q |_{\text{cross}} . \tag{63}$$

The data in Figs. 5–8 for the individual linear terms, for $| L |_{\text{init}}$ and $| L |_k$, and for $| Q |_{\text{init}}$ and $| Q |_k$ is now self evident. Briefly, in Fig. 5, for $| \Delta O/O |$ the initial value of [O] is seen not to be a factor at times greater than 10^{-5} hr, whereas the initial value of $[O_3]$ is a sensitive parameter from 10^{-6} hr to late times of 10^2–10^3 hr. The initial value of $[O_2]$ is seen to be a sensitive parameter from 10^{-4} hr to late times. The corresponding quadratic terms $| Q |_{\text{init}}$, are seen to be sensitive parameters at times later than 10^{-4} hr for all $| \Delta c/c |$ greater than approximately 0.25 (recall the quadratic and linear scaling). In Fig. 6; for $| \Delta O_3/O_3 |$; the initial value of [O] never appears to be a factor, while the initial value of $[O_3]$ is a sensitive parameter out to approximately 10^2 hr. The initial value of $[O_2]$ assumes importance, starting at about 10^2 hr, onward. The corresponding quadratic terms, $| Q |_{\text{init}}$, for $| \Delta c/c | = 1$ start to become significant only at times greater than 10^3 hr.

Following the same lines of observation, analogous interpretations can be made of the rate coefficient sensitivities in Figs. 7 and 8 for $| \Delta O/O |$ and $| \Delta O_3/O_3 |$. Without belaboring that portion of the discussion further, it is very interesting to note that asymptotic limits of 0.5 were approached for all of the individual linear sensitivity coefficients $| a_i |$, for both $| \Delta O/O |$ and $| \Delta O_3/O_3 |$. That this should be true was indeed verified by an independent algebraic solution of the appropriate *steady state* sensitivity equations. This indicates that even the very weak rates in a system eventually assume sensitivity importance, and the modeller should be aware of those time scales.

Finally, sensitivities associated with the time varying diurnal rate calculations (for $k_3(t)$ and $k_4(t)$ under Type 3, above) were computed. Recall that the functional derivatives used in sensitivity analysis of time dependent parameters are dependent upon the functions $g_i(t)$ (see Eqs. 52–56). Thus, a one-to-one comparison of diurnal sensitivity results to the constant rate results can only be attempted for parameters that do not vary in time. These are the initial conditions and the rates k_1 and k_2.

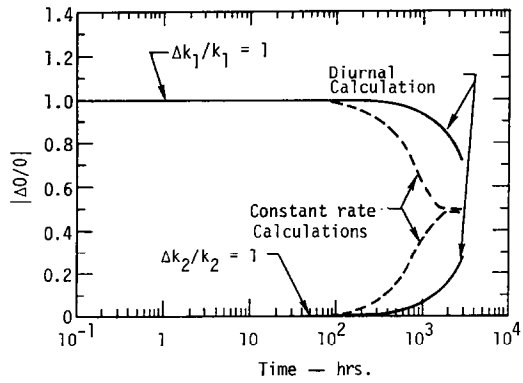

FIG. 9. Linear sensitivity to k_1 and k_2 for $|\Delta O/O|$ in constant rate and in diurnal calculations.

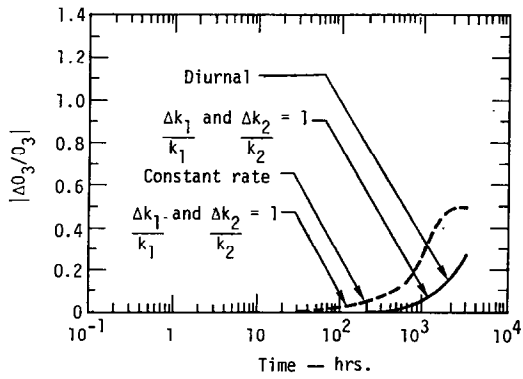

FIG. 10. Linear sensitivity to k_1 and k_2 for $|\Delta O_3/O_3|$ in constant rate and in diurnal calculations.

Inasmuch as the reaction rate sensitivities are normally the most interesting, Figs. 9 and 10 show the linear sensitivities of [O] and [O_3] to k_1 and k_2 for both the constant rate and diurnal calculations. Clearly, the mechanistic sensitivities are qualitatively disparate after about 10^2 hr, and the approach to asymptotic conditions occurs at significantly later times for the diurnal calculations than for the constant rate calculations. (It gets very expensive to run diurnal calculations to problem times exceeding a few thousand hours.) The sensitivity of [O] to the time varying rates $k_3(t)$ and $k_4(t)$ are of the same saw tooth nature as [O] itself (as shown in Fig. 1). That is, sizable sensitivities occur during daylight hours, and negligible sensitivities to $k_3(t)$ and $k_4(t)$ occur for $|\Delta O/O|$ at night.

Clearly, this alternating sensitivity encountered in the diurnal mechanism generates the differing dependencies on the legitimately constant rate coefficients

k_1 and k_2 for $|\Delta O_3/O_3|$, which does not respond instantaneously, as well as for $|\Delta O/O|$, which does respond instantaneously to solar flux variations. The significance of these results undoubtedly bears heavily upon more complex kinetic mechanisms in which numerous free radicals and reactive intermediates may be important. Results presented in an earlier study of a complex diurnal atmospheric system by Gelinas [8] tend to be consistent with the detailed, but simplified, sensitivity results of the present article.

The computer code used for the calculations described here uses a variable-step variable-order stiff ODE solver called EPISODE [9, 10].

V. Summary

The DM approach taken to sensitivity analysis in this paper is but one of a few approaches that are emerging into current practice. Each approach has its individual mertis and its commonalities with other approaches. Accordingly, the choice of a particular method for specific examples tends to be very much a problem-dependent matter at this time.

In this article, a number of factors have been emphasized. Basically, we have written for the scientific practitioner. The uncertainties, Δy_i, are viewed simply as random variables rather than dealing with the expectation values $\langle \Delta y_i \rangle$ and $\langle (\Delta y_i)^2 \rangle$. All are useful quantities and are complementary in applications. Our particular choice is useful for the types of questions in physical modeling that require worst case estimates of sensitivities to uncertain reaction rate processes with unknown statistical properties. Indeed, by the time statistical properties of rate data becomes available some of the most pressing scientific needs for sensitivity analysis may have diminished.

We have also included computational information to potential users of this method that will allow them to extend their existing kinetics codes to solve for sensitivity variables simultaneously with species concentrations. This method has been entirely automated to the point that the user simply inputs his reaction numbers and initial conditions. The fully general, nonlinear (in y_i), coupled species and sensitivity equation compilation and solution is automatically performed without further user intervention. A particularly potent feature is that sensitivities to both constant and time varying parameters is readily performed continuously for all times t, in a solution history. Second-order terms also can be readily evaluated in the present sensitivity analysis, although it is a tedious process.

An illustrative example of the Chapman kinetic mechanism for atmospheric ozone formation has been presented. Two basic cases were solved: (1) photodissociation rates were held constant at their appropriate daily averaged values, and (2) diurnally varying photodissociation rates were used. The results of these

calculations show the sensitivity distinctions between diurnal driving mechanisms and constant, daily averaged kinetic mechanisms. In addition to the transient discrepancies between the two types of calculations, the approach to asymptotic states was also quite different for the two types of calculations, clearly implying a need for closer examination of constant solar flux approximations that are commonly used in atmospheric applications. The times at which the very weak reaction processes became significant in these solution histories was also quite evident.

Finally, the quantitative comparison of second-order terms to the linear sensitivity terms strongly indicates the need for more higher-order analysis in the future. In the present work, the very reactive specie, O, was found to be most subject to higher-order effects and to diurnal deviations from constant rate mechanistics. There is a clear suggestion from these results that the very reactive species, such as free radicals, should be treated with due consideration of their mechanistic impact on the total system.

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