

# SENSITIVITY ANALYSIS IN ChE EDUCATION

## Part 1. Introduction and Application to Explicit Models\*

WILLIAM R. SMITH,\*\* RONALD W. MISSEN\*\*\*  
University of Guelph • Guelph, Ontario, Canada N1G 2W1

Engineering analysis and design typically proceed by construction of system models, followed by incorporation of required input quantities and the solution of the model equations to obtain values of output quantities of interest. The construction of models is an important aspect of engineering pedagogy, as is familiarity with numerical methods of solution for their more complex forms.<sup>[1]</sup> In addition to teaching students to construct and solve models for their outputs, we believe it is also important to emphasize consideration of the effects on outputs when input quantities are subject to variability and/or uncertainty. This is accomplished by sensitivity analysis (SA), which can be defined as the study of the uses of, and methodologies for, quantitatively calculating the effects of changes in input quantities on model outputs, especially for a large number of inputs. (Of course, one can directly calculate values of output quantities as functions of input quantities, but this only reveals sensitivities qualitatively and is only satisfactory when the number of inputs is small, say,  $\leq 3$ ). In addition, a broad pedagogical use of SA is to provide a unifying theme for the study and understanding of topics arising in a number of areas in chemical engineering.

The fundamental concepts of SA are accessible to students who have a basic background in multivariable calculus, but full development requires some knowledge of linear algebra, which may not be a requirement in all undergraduate programs. Thus, although some concepts can be introduced in the undergraduate curriculum, the full treatment is more appropriate at the graduate level.

In chemical engineering, SA has a tradition of importance in the field of optimization.<sup>[2,3]</sup> Our own experience with SA has been principally in equilibrium models for chemically reacting systems,<sup>[4-6]</sup> which can be considered as optimization problems. In recent chemical engineering literature, SA

has been applied to the design of reactive distillation units<sup>[7]</sup> and to process simulator models.<sup>[8]</sup> Varma, *et al.*, have considered SA in the context of chemical reactor models and related situations,<sup>[9]</sup> and a recent general treatment of SA (not specifically oriented to chemical engineering) was given by Saltelli, *et al.*<sup>[10]</sup>

Questions addressed by SA in a broad sense include

1. What are appropriate quantitative measures of sensitivity of model outputs to changes in inputs? Particular measures addressing this question involve the marginal rates of change or marginal sensitivities of each output with respect to each input. These particular measures include the following items, which form the basis of this paper:
  - a. A measure of the relative importance of each input for a given output is the relative value of the output's marginal sensitivity with respect to each input.
  - b. A measure of the uncertainties in model outputs

**William R. Smith** is Professor of Engineering and of Mathematics and Statistics at the University of Guelph. He received his BSc and MSc in chemical engineering from the University of Toronto and his MSc and PhD degrees in applied mathematics from the University of Waterloo. His research is in classical and statistical thermodynamics. He is coauthor of *Chemical Reaction Equilibrium Analysis* (1982, 1991).



**Ronald W. Missen** is Professor Emeritus (chemical engineering) at the University of Toronto. He received his BSc and MSc degrees in chemical engineering from Queen's University and his PhD in physical chemistry from the University of Cambridge. He is coauthor of *Chemical Reaction Equilibrium Analysis* (1982, 1991) and *Introduction to Chemical Reaction Engineering and Kinetics* (1999).

\* Part 2 will be published in the Fall issue of CEE.

\*\* Present address: University of Ontario Institute of Technology, Oshawa, Ontario, Canada L1H 7K4

\*\*\* University of Toronto, Toronto, Ontario, Canada M5S 3E5

that result from uncertainties in the inputs. In general, this matter is called uncertainty analysis, and international bodies have published documents describing standards for the expression of such uncertainties.<sup>[11,12]</sup> Uncertainty analysis is also discussed in some undergraduate texts.<sup>[13-16]</sup>

- c. A measure of the overall effects on the outputs of changes in combinations of inputs. This measure shows the relative importance of particular combinations of inputs.
2. What is the direction of change (sign) of outputs for a specified direction of input changes, given only the model structure (i.e., without obtaining a solution)?
3. Is there a large qualitative change in the outputs for small input changes?
4. Do the outputs change significantly when the underlying assumptions of the model change?

Question 1 is usually considered to be the primary scope of SA, but it may include Question 4,<sup>[10]</sup> and we add Questions 2 and 3 as being in the same spirit and further broadening its scope. Question 2 is important in requiring only a minimal amount of model information (signs of quantities) as, for example, in a form of Le Chatelier's Principle.<sup>[17]</sup> Question 3 arises, for example, in the context of models described by differential equations and is addressed by stability and bifurcation theory.<sup>[18]</sup> A chemical engineering example concerns finding circumstances under which a chemical reactor changes its behavior from steady state to periodic.

Question 4 arises in statistics; the term *robustness* refers to the effects on a statistical analysis of changing the assumptions concerning underlying probability distributions.<sup>[19]</sup> Another chemical engineering example concerns situations when parameters in models are estimated from experimental data, requiring assumptions regarding measurement errors. It is desirable that the resulting parameter values do not depend strongly on departures from such assumptions.

In these two papers (Parts 1 and 2), we focus on only the first question. In this paper (Part 1), we introduce SA, describe two different classes of engineering models, and apply SA to address items 1a, 1b, and 1c for one of these classes. In Part 2, we will apply SA to the same items for the other class of model. Conclusions, including what is appropriate for the undergraduate curriculum and what can be deferred to the graduate curriculum, will be given at the end of Part 2.

In the following sections, we first describe two types of inputs and two types of models. For one type of model, we then consider, in turn, item 1a for both types of inputs, 1b for one type of input, and 1c for the other type of input (although, in principle, all three items could be considered for both types of inputs).

The reasons for applying items 1b and 1c to different input quantities are: we are usually interested in determining the effects on the outputs of uncertainties in the type considered

for specified values of the other inputs (item 1b); conversely, we are usually interested in determining the effects on the outputs of changes in inputs over which the designer has control (item 1c). We will conclude with a pressure drop example for numerical illustration.

The treatment we describe and the examples we use in both Parts 1 and 2 relate to models that are amenable to analytical treatment to obtain values of the sensitivity quantities involved. The methodology, however, is not limited to such cases. In very complicated situations involving many variables, it may be possible to use computer algebra software to obtain values, and if necessary, values can be obtained by numerical differentiation, e.g., using a process simulator.

## **TYPES OF MODEL INPUTS SYSTEM VARIABLES AND CONSTITUTIVE PARAMETERS**

It is useful to consider two different types of input quantities in models: *system variables* ( $x_j$ ,  $j = 1, 2, \dots, J$ ) and *constitutive parameters* ( $p_k$ ,  $k = 1, 2, \dots, K$ ). System variables (such as temperature,  $T$ , and pressure,  $P$ ) are input quantities that can be manipulated by the designer or are imposed by the external environment; their values are usually considered to be specified precisely, but they may be subject to change. Constitutive parameters (such as viscosity and thermal conductivity) are those that must be obtained externally to the model, either by direct measurement or from correlations; their values are usually subject to uncertainties.

## **TYPES OF MODELS EXPLICIT AND IMPLICIT**

It is also useful to consider two different types of models that arise in engineering—explicit and implicit models, terms that denote mathematically how the outputs are available from the model in terms of the inputs. In principle, we can also consider further model classifications involving, for example, continuous versus discrete variables, and deterministic versus stochastic models. Here, however, we treat only the simplest situation of a deterministic model involving continuous variables, and we further assume that any functions involved in the models are differentiable. Although SA can be used for more complex situations, the methodology is correspondingly more complex. Furthermore, continuous-variable and differentiable deterministic models constitute a large class of engineering models.

An explicit model with  $N$  outputs,  $y_i$ , is one that can be written

$$y_i = f_i(\mathbf{x}; \mathbf{p}); \quad i = 1, 2, \dots, N \quad (1)$$

where  $\mathbf{x}$  is the vector of  $J$  system variables and  $\mathbf{p}$  is the vector of  $K$  constitutive parameters. A simple example is a pressure-explicit three-parameter equation of state (EOS), with output quantity  $P$ , system variables molar volume ( $v$ ) and  $T$ ,

and constitutive parameters critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and acentric factor ( $\omega$ )

$$P = P(v, T; T_c, P_c, \omega) \quad (2)$$

A more complex class of models is that of implicit models, which arise when the output quantities are implicit functions of the inputs, expressed formally as

$$f_i(y, x; p) = 0; \quad i = 1, 2, \dots, N \quad (3)$$

where  $y$  is the vector of outputs. Implicit models can take many forms. Their distinguishing property is that Eq. (3) cannot be “solved analytically” for  $y_i$  (although it is usually assumed that the solution of the equations is unique). A simple example of an implicit model arises in the context of a pressure-explicit EOS when  $v$  is the output quantity and  $(P, T)$  are system variables; then  $v(T, P)$  is defined implicitly by

$$P - P[v(T, P), T; T_c, P_c, \omega] = 0 \quad (4)$$

More complex examples of implicit models include sets of nonlinear algebraic or transcendental equations, systems of differential equations (ordinary or partial), and optimization models.

The details of SA methodology are different for explicit and implicit models, but the general mathematical tools are similar. In Part 1, we will consider applications of SA to explicit models, while deferring implicit models to Part 2.

## SENSITIVITY COEFFICIENTS

Fundamental quantities used in SA are the marginal rates of change of output quantities in the model in terms of input quantities, *i.e.*, their (partial) derivatives. This addresses item 1a. The first derivatives  $\partial y_i / \partial x_j$  and  $\partial y_i / \partial p_k$  are called *first-order sensitivity coefficients*. The *normalized* first-order sensitivity coefficients are  $\partial \ln y_i / \partial \ln x_j$  and  $\partial \ln y_i / \partial \ln p_k$ , which have the advantage that their values are independent of the units used. Furthermore a normalized coefficient can be interpreted as the % change in the output  $y_i$  for a 1% change in the input  $x_j$  or  $p_k$ . The two types of coefficient are related by

$$\frac{\partial \ln y_i}{\partial \ln x_j} \equiv \frac{x_j}{y_i} \left( \frac{\partial y_i}{\partial x_j} \right) \quad i = 1, 2, \dots, N \quad j = 1, 2, \dots, J \quad (5)$$

$$\frac{\partial \ln y_i}{\partial \ln p_k} \equiv \frac{p_k}{y_i} \left( \frac{\partial y_i}{\partial p_k} \right) \quad i = 1, 2, \dots, N \quad k = 1, 2, \dots, K \quad (6)$$

In some situations, it is appropriate to consider second derivatives as *second-order sensitivity coefficients*,  $\partial^2 y_i / \partial x_j^2$ ,  $\partial^2 y_i / \partial p_k^2$ , and corresponding normalized forms.

### ■ ITEM 1a

#### Relative Importance of Changes in Input Quantities

To address item 1a, a measure of the relative importance of

each input (*i.e.*, each system variable and each constitutive parameter) on each output is the absolute value of the relevant sensitivity coefficient, as shown below.

The effects of small changes in the inputs on the outputs can be approximated by a Taylor expansion using the first-order sensitivity coefficients of the outputs with respect to the inputs

$$\delta y_i = \sum_{j=1}^J \left( \frac{\partial y_i}{\partial x_j} \right) \delta x_j + \sum_{k=1}^K \left( \frac{\partial y_i}{\partial p_k} \right) \delta p_k \quad i = 1, 2, \dots, N \quad (7)$$

In order to consider all outputs and inputs on the same (relative) basis, the logarithmic form of Eq. (7) can be used:

$$\frac{\delta y_i}{y_i} \equiv \delta \ln y_i = \sum_{j=1}^J \left( \frac{\partial \ln y_i}{\partial \ln x_j} \right) \delta \ln x_j + \sum_{k=1}^K \left( \frac{\partial \ln y_i}{\partial \ln p_k} \right) \delta \ln p_k \quad i = 1, 2, \dots, N \quad (8)$$

For a given value of each input change, the relative importance of each input on the magnitude of each output is the magnitude of the relevant sensitivity coefficient.

### ■ ITEM 1b

#### Effects of Constitutive Parameter Changes on Outputs: Uncertainty Analysis

Here we use the sensitivity coefficients with respect to the constitutive parameters to address item 1b, since uncertainty analysis concerns the effects on outputs of uncertainties in these parameters.

The (standard) uncertainty of measurement of a quantity,  $w_i$ , is an associated quantity,  $u(w_i)$ , that characterizes the dispersion of the measured values that could reasonably be ascribed to the quantity.<sup>[11]</sup>  $u(w_i)$  is taken as the square root of the variance,  $\sigma_i^2$ , if this is available, and approximate 95% uncertainty limits (assuming the uncertainties arise from a normal distribution with zero mean) for  $w_i$  are then  $(w_i - 2u(w_i), w_i + 2u(w_i))$ . (If  $\sigma_i^2$  is unavailable, an estimate of  $u(w_i)$  must be used.<sup>[11]</sup>)

We identify the average value of  $\delta y_i^2$  or  $(\delta \ln y_i)^2$  obtained from Eq. (7) or (8) with  $\sigma^2(y_i)$  or  $\sigma^2(\ln y_i)$ , respectively, with analogous identifications for the covariances. In terms of uncertainties, this yields

$$u^2(y_i) = \sum_{j=1}^K \left( \frac{\partial y_i}{\partial p_j} \right)^2 u^2(p_j) + \sum_{j=1}^K \sum_{k \neq j=1}^K \left( \frac{\partial y_i}{\partial p_j} \right) \left( \frac{\partial y_i}{\partial p_k} \right) u(p_j, p_k) \quad i = 1, 2, \dots, N \quad (9)$$

where  $u(p_j, p_k)$  is the joint uncertainty of  $p_j$  and  $p_k$ . When the constitutive parameters are uncorrelated (the typical case), the last part of Eq. (9) is absent. In this case, the relative

importance of each parameter is given by the square of the relevant sensitivity coefficient. An expression analogous to Eq. (9) can be written in terms of relative uncertainties. We note that  $u(\ln y_i) \equiv u(y_i)/y_i$ , which represents the relative uncertainty in  $y_i$  (and correspondingly for  $p_j$ ). Reporting numerical values of uncertainties in such a standard way, in addition to values of the quantities themselves, is an emerging requirement.<sup>[11,12]</sup>

## ITEM 1c

### Overall Effects of System Variable Changes on Outputs

To address item 1c, we consider only the system variables, which (unlike the constitutive parameters) are normally under the control of the investigator. The sum of squares of the changes in the model outputs for given changes in the system variables is an appropriate overall measure. In what follows, we give expressions in terms of the sensitivity coefficients themselves; corresponding expressions can be written in terms of the normalized sensitivity coefficients (Eqs. 5 and 6). The change in the overall sum of squares due to small system variable changes is given from Eq. (7) by

$$\delta S = \sum_{i=1}^N \delta y_i^2 = \sum_{j=1}^J \sum_{k=1}^J P_{jk} \delta x_j \delta x_k \quad (10)$$

where  $P_{jk}$  are entries in a matrix  $\mathbf{P}$ :

$$P_{jk} = \sum_{i=1}^N \left( \frac{\partial y_i}{\partial x_j} \right) \left( \frac{\partial y_i}{\partial x_k} \right) \quad j, k = 1, 2, \dots, J \quad (11)$$

For a given  $\delta \mathbf{x}$ ,  $\delta S$  can be calculated from Eq. (10), but further insight can be obtained by expressing  $\delta S$  in a simpler form in terms of a new set of system change variables,  $\delta \boldsymbol{\theta}$ , as follows. The right side of Eq. (10) is a quadratic sum of the system variable changes, and it is a standard exercise in linear algebra to express this as a weighted sum of squares.<sup>[20]</sup> This is essentially the approach used by Seferlis and Grievink in design and sensitivity analysis for reactive distillation.<sup>[7]</sup>

An arbitrary change vector  $d\mathbf{x}$  can be expressed in terms of a set of normalized (*i.e.*, in the mathematical sense of unit length) linearly independent eigenvectors of  $\mathbf{P}$ ,  $\{\mathbf{z}_j, j=1, 2, \dots, J\}$ , via

$$\delta \mathbf{x} = \sum_{j=1}^J \mathbf{z}_j \delta \theta_j \quad (12)$$

where  $\delta \theta_j$  is the coordinate of  $\delta \mathbf{x}$  with respect to  $\mathbf{z}_j$ . We then express  $\delta S$  in Eq. (10) in the simplified form

$$\delta S = \sum_{i=1}^N \sum_{j=1}^J \sum_{k=1}^J \sum_{\ell=1}^J \mathbf{z}_k^T \mathbf{P} \mathbf{z}_\ell \delta \theta_k \delta \theta_\ell = \sum_{j=1}^J \lambda_j \delta \theta_j^2 \quad (13)$$

where  $\lambda_j$  (which is non-negative<sup>[20]</sup>) is an eigenvalue of  $\mathbf{P}$  cor-

responding to  $\mathbf{z}_j$ . Equation (10) represents a  $J$ -dimensional ellipsoid involving the variables  $\delta \mathbf{x}$  for a given value of  $\delta S$ . Equation (13) expresses this ellipsoid in “standard form” in terms of the new variable  $\delta \boldsymbol{\theta}$ . Equation (12) resolves  $\delta \mathbf{x}$  into its coordinates in terms of the new coordinate directions  $\mathbf{z}_j$ .

Equations (12) and (13) show that if  $\delta \mathbf{x}$  is proportional to an individual eigenvector  $\mathbf{z}_j$ ,  $\delta S$  is given by the product of the square of the proportionality constant  $\delta \theta_j$  and the corresponding eigenvalue  $\lambda_j$ . We can thus assess the relative importance of changes of  $\delta S$  from a nominal value in the direction of each eigenvector by ordering the eigenvalues of  $\mathbf{P}$ .

## EXAMPLE

### Pressure Drop in a Fixed-Bed Reactor

A fixed-bed catalytic chemical reactor consists of a bed of catalyst particles through which the reacting system flows. As part (for a simple illustration) of the overall design/analysis of such a reactor, we consider an explicit model that approximates the pressure drop ( $-\Delta P$ ) of a fluid flowing through a cylindrical bed of spherical particles:<sup>[21]</sup>

$$(-\Delta P) = \frac{64}{\pi^3} \left( \frac{1 - \epsilon_B}{\epsilon_B^3} \right) \frac{\dot{m}^2 V}{\rho_f d_p D^6} \left[ 1.75 + \frac{150(1 - \epsilon_B) \pi \mu_f D^2}{4 \dot{m}_p} \right] = f_1(1.75 + f_2) \quad (14)$$

where

$$f_1 = \frac{64}{\pi^3} \left( \frac{1 - \epsilon_B}{\epsilon_B^3} \right) \frac{\dot{m}^2 V}{\rho_f d_p D^6} \quad (15)$$

$$f_2 = \frac{150(1 - \epsilon_B) \pi \mu_f D^2}{4 \dot{m}_p} \quad (16)$$

where

- V bed volume
- D bed volume diameter
- u superficial linear fluid velocity
- $\rho_f$  fluid density
- $d_p$  particle diameter
- $\epsilon_B$  bed voidage
- $\mu_f$  fluid viscosity
- m mass flow rate through the bed.

The values at the reactor inlet are  $\rho_f$  and  $\mu_f$ . The bed depth,  $L$ , is given by

$$L = \frac{4V}{\pi D^2} \quad (17)$$

Equations (14) and (17) constitute an explicit model for the output quantities  $\{(-\Delta P), L\}$  in terms of the system vari-

ables  $\{D, V, \dot{m}\}$  and the constitutive parameters  $\{\epsilon_B, d_p, \rho_f, \mu_f\}$ . For this example,  $N = 2$ ,  $J = 3$ , and  $K = 4$ .

Expressions for the first-order sensitivity coefficients, together with the corresponding normalized coefficients are given in Table 1; the numerical values shown are obtained from the following data, relating to the first stage of a particular sulfur dioxide converter.<sup>[21]</sup>

$$D = 4.31 \text{ m}; \quad V = 12 \text{ m}^3; \quad \dot{m} = 38.0 \text{ kg s}^{-1};$$

$$\rho_f = 0.548 \text{ kg m}^{-3}; \quad \mu_f = 3.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1};$$

$$d_p = 0.015 \text{ m}; \quad \epsilon_B = 0.45$$

From these data,  $f_1 = 4097 \text{ kg m}^{-1} \text{ s}^{-2}$  ( $\equiv \text{Pa}$ ) and  $f_2 = 0.08024$ .

With regard to item 1a, Column 4 of Table 1 indicates that the most important system variable affecting changes (in an absolute sense) in both  $(-\Delta P)$  and in  $L$  is  $D$ ; the most important constitutive parameter in this sense affecting  $(-\Delta P)$  appears to be  $\mu_f$ ;  $L$  is independent of all the constitutive parameters.

For relative changes, Column 5 indicates that the most important system variable for both  $(-\Delta P)$  and  $L$  is also  $D$ ; the most important constitutive parameter for  $(-\Delta P)$  is  $\epsilon_B$ . Of these two types of comparison, that involving normalized quantities is more informative, since the coefficients are independent of the units.

To gain further insight concerning the dependence of the outputs on the inputs, we calculate the sensitivity coefficients as functions of the input quantities. For example, since the most important system variable is  $D$ , we show in Figure 1 the relative sensitivity coefficients of  $(-\Delta P)$  as functions of  $D$ . They are all weak functions of  $D$ , and their relative importance does not change appreciably from that at the conditions of the problem statement, indicated by intersections with

the vertical line at 4.31 m.

For item 1b, from the values in Column 5 of Table 1, the uncertainty in  $\ln(-\Delta P)$  in terms of the uncertainties in the constitutive parameters is given by the normalized version of Eq. (9) as

$$u^2[\ln(-\Delta P)] = u^2(\ln \rho_f) + (0.0438)^2 u^2(\ln \mu_f) + (1.044)^2 u^2(\ln d_p) + (3.854)^2 u^2(\ln \epsilon_B) \quad (18)$$

where the covariances are assumed to be zero (a typical case). This further indicates the relative importance of the variable  $\epsilon_B$ . Equation (18) requires values of the uncertainties in the constitutive parameters,  $u(p_i)$ , as described under item 1b.

**TABLE 1**  
Nonzero\* First-Order Sensitivity Coefficients for the Pressure Drop Example\*\*

Coefficient	Expression for Coefficient (A) (from Eqs 14-17)	Expression for Normalized Coefficient (B) (from Eqs. 5-6)	Value of (A)	Value of (B)
$\frac{\partial(-\Delta P)}{\partial D}$	$-\frac{f_1}{D}(10.5 + 4f_2)$	$-2\left(\frac{5.25 + 2f_2}{1.75 + f_2}\right)$	-10.29 kPa m <sup>-1</sup>	-5.912
$\frac{\partial(-\Delta P)}{\partial V}$	$\frac{f_1}{V}(1.75 + f_2)$	1	0.625 kPa m <sup>-3</sup>	1
$\frac{\partial(-\Delta P)}{\partial \dot{m}}$	$\frac{f_1}{\dot{m}}(3.5 + f_2)$	$\left(\frac{3.50 + f_2}{1.75 + f_2}\right)$	0.386 kPa s kg <sup>-1</sup>	1.956
$\frac{\partial(-\Delta P)}{\partial \rho_f}$	$-\frac{f_1}{\rho_f}(1.75 + f_2)$	-1	-13.7 kPa m <sup>3</sup> kg <sup>-1</sup>	-1
$\frac{\partial(-\Delta P)}{\partial \mu_f}$	$\frac{f_1 f_2}{\mu_f}$	$\frac{f_2}{1.75 + f_2}$	8650 kPa m s kg <sup>-1</sup>	0.0438
$\frac{\partial(-\Delta P)}{\partial d_p}$	$-\frac{f_1}{d_p}(1.75 + 2f_2)$	$-\left(\frac{1.75 + 2f_2}{1.75 + f_2}\right)$	-522 kPa m <sup>-1</sup>	-1.044
$\frac{\partial(-\Delta P)}{\partial \epsilon_B}$	$-\frac{f_1}{\epsilon_B(1 - \epsilon_B)} \times [1.75(3 - 2\epsilon_B) + (3 - \epsilon_B)f_2]$	$-\left[3 + \left(\frac{\epsilon_B}{1 - \epsilon_B}\right)\left(\frac{1.75 + 2f_2}{1.75 + f_2}\right)\right]$	-64.2 kPa	-3.854
$\frac{\partial L}{\partial D}$	$-\frac{8V}{\pi D^3}$	-2	-0.3817	-2
$\frac{\partial L}{\partial V}$	$\frac{4}{\pi D^2}$	1	0.06854 m <sup>-2</sup>	1

\*  $\frac{\partial L}{\partial \dot{m}} = \frac{\partial L}{\partial \rho_f} = \frac{\partial L}{\partial \mu_f} = \frac{\partial L}{\partial d_p} = \frac{\partial L}{\partial \epsilon_B} = 0$

\*\*  $f_1 = 4.097 \text{ Pa}$ ;  $f_2 = 0.08024$ ;  $f_1$  and  $f_2$  are defined by Eqs. 14 and 15.

For example, a 1% relative uncertainty in each parameter results in a relative uncertainty in  $(-\Delta P)$  of 4.1%.

For item 1c, to assess the overall effects of relative changes in the system variables on relative changes of the outputs, the equivalent of the matrix  $\mathbf{P}$  defined in Eq. (11) in terms of normalized sensitivity coefficients is calculated from the values in Column 5 of Table 1:

$$\mathbf{P} = \begin{pmatrix} 38.955 & -7.912 & -11.565 \\ -7.912 & 2 & 1.956 \\ -11.565 & 1.956 & 3.827 \end{pmatrix} \quad (19)$$

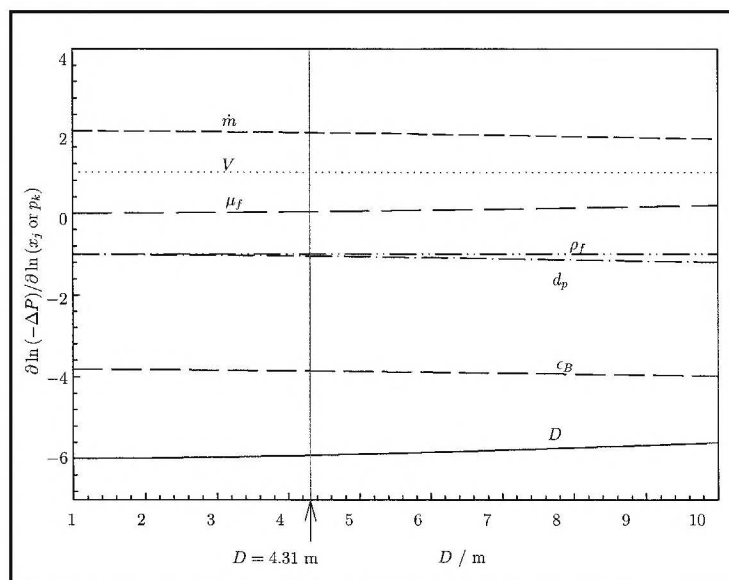
The eigenvalues of  $\mathbf{P}$ ,  $\lambda_i$ , and their normalized eigenvectors,  $\mathbf{z}_i$ , are<sup>[22]</sup>

$$\left. \begin{aligned} \lambda_1 &= 43.999; & \mathbf{z}_1 &= (0.941, -0.190, -0.280)^T \\ \lambda_2 &= 0.783; & \mathbf{z}_2 &= (0.060, -0.721, 0.691)^T \\ \lambda_3 &= 0; & \mathbf{z}_3 &= (0.333, 0.667, 0.667)^T \end{aligned} \right\} \quad (20)$$

The normalized equivalent of Eq. (13) gives

$$\delta \ln S \equiv [\delta \ln(-\Delta P)]^2 + [\delta(\Delta \ln L)]^2 = 43.999 \delta\theta_1^2 + 0.783 \delta\theta_2^2 + 0\delta\theta_3^2 \quad (21)$$

This indicates that, when a change vector for the system variables  $(\delta \ln D, \delta \ln V, \delta \ln \dot{m})^T$  is proportional to an individual eigenvector  $\mathbf{z}_i$  (with proportionality constant  $\delta\theta_i$ ), the relative change in  $S$  ( $\delta \ln S$ ) is given by  $\lambda_i \delta\theta_i^2$ . Since  $\lambda_1 = 43.999$  is the largest eigenvalue, Eq. (21) indicates that the largest relative change in  $S$  occurs in the direction of  $\mathbf{z}_1$ . For example, a unit change of the system variables  $(\delta \ln D, \delta \ln V, \delta \ln \dot{m})^T$  in the direction of  $\mathbf{z}_1$  leads to a 44-fold relative change



**Figure 1.** Pressure drop example: Normalized sensitivity coefficients for  $(-\Delta P)$  as functions of bed diameter  $D$ ; values at  $D = 4.31$  m correspond to those in Table 1.

in  $S$ . Note also that there is one zero eigenvalue; in general, when  $N \leq J$ , the number of zero eigenvalues is at least  $J - N$ . For a system variable change vector proportional to  $\mathbf{z}_3$  (corresponding to  $\lambda_3 = 0$ ), the relative change in  $S$  is zero.

## ACKNOWLEDGMENT

Financial assistance has been received from the Natural Sciences and Engineering Research Council of Canada.

## REFERENCES

1. Cutlip, M., and M. Shacham, *Problem Solving in Chemical Engineering with Numerical Methods*, Prentice-Hall PTR, Upper Saddle River, NJ (1998)
2. Fiacco, A.V., *Introduction to Sensitivity and Stability Analysis in Nonlinear Programming*, Academic Press, New York, NY (1983)
3. Edgar, T.F., D.M. Himmelblau, and L.S. Lasdon, *Optimization of Chemical Processes*, 2nd ed., McGraw-Hill, New York, NY (2001)
4. Smith, W.R., *Can. J. Chem. Eng.*, **47**, 95 (1969)
5. Smith, W.R., and R.W. Missen, *Chemical Reaction Equilibrium Analysis*, Chapter 8, Wiley-Interscience, New York, NY (1982); Krieger, Malabar, FL (1991)
6. Norval, G.W., M.J. Phillips, R.W. Missen, and W.R. Smith, *Can. J. Chem. Eng.*, **67**, 652 (1989); *Appl. Catal.*, **54**, 37 (1989); *Ind. Eng. Chem. Res.*, **28** 1884 (1989)
7. Seferlis, P., and J. Grievink, *Ind. Eng. Chem. Res.*, **40**, 1673 (2001)
8. Xin, Y., and W.B. Whiting, *Ind. Eng. Chem. Res.*, **39**, 2998 (2000)
9. Varma, A., M. Morbidelli, and H. Wu, *Parametric Sensitivity in Chemical Systems*, Cambridge University Press (1999)
10. Saltelli, A., K. Chan, and E.M. Scott, *Sensitivity Analysis*, John Wiley & Sons, New York, NY (2000)
11. *European Cooperation for Accreditation of Laboratories*, Report EAL-R2, 27pp. (1997)
12. <<http://physics.nist.gov/Pubs/guidelines/contents.html>>
13. Figlio, R.R., and D.E. Beasley, *Theory and Design for Mechanical Measurements*, Chapter 5, John Wiley & Sons, New York, NY (1991)
14. Holman, J.P., *Experimental Methods for Engineers*, 6th ed., pp. 49-56, McGraw-Hill, New York, NY (1994)
15. Taylor, J.R., *An Introduction to Error Analysis*, 2nd ed., University Science Books, Sausalito, CA (1997)
16. Coleman, H.W., and W.G. Steele, *Experimentation and Uncertainty Analysis for Engineers*, 2nd ed., John Wiley & Sons, New York, NY (1999)
17. Le Chatelier, H., *Compt. rend.*, **99**, 786 (1884); **100**, 50 (1885); **196**, 1557 (1933); *Ann. des Mines, Sér. 8*, **13**, 157, 200, 362 (1988)
18. See, for example, Boyce, W.E., and R.C. DiPrima, *Elementary Differential Equations and Boundary Value Problems*, 7th ed., Chapter 9, John Wiley & Sons, New York, NY (2001)
19. Huber, P.J., *Robust Statistics*, John Wiley & Sons, New York, NY (1981)
20. Anton, H., and C. Rorres, *Elementary Linear Algebra, Applications Version*, 7th ed., pp. 483-485, John Wiley & Sons, New York, NY (1994)
21. Missen, R.W., C.A. Mims, and B.A. Saville, *Introduction to Chemical Reaction Engineering and Kinetics*, pp. 516-519, John Wiley & Sons, New York, NY (1999)
22. MAPLE is a registered trademark of Waterloo Maple, Inc. □