Reliable Nonlinear Parameter Estimation Using Interval Analysis: Error-in-Variable Approach[†]

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Abstract: Parameter estimation is a key problem in the development of process models, both steady- and unsteady-state, and thus is an important issue in both process design and control. The error-in-variable approach differs distinctly from the standard approach in that measurement errors in both dependent and independent system variables are taken into account when formulating the objective function in the parameter estimation problem. It is not uncommon for the objective function in nonlinear parameter estimation problems to have multiple local optima. However, the usual methods used to solve these problems are local methods that offer no guarantee that the global optimum, and thus the best set of model parameters, has been found. We demonstrate here a technique, based on interval analysis, that can solve the error-in-variable parameter estimation problem with complete reliability, providing a mathematical and computational guarantee that the global optimum is found. As examples, we consider the estimation of parameters in both steady and unsteady-state models, including a vapor-liquid equilibrium (VLE) model, a CSTR model, and a reaction kinetics model.

Keywords: Parameter Estimation, Modeling, Error-in-Variable Method, Global Optimization, Interval Analysis

1 Introduction

The mathematical modeling of physical phenomena is a core aspect of the simulation and optimization tools used for purposes of chemical process design and control. The features and accuracy of the models used determine the realism with which the actual process can be represented. Use of appropriate models is helpful not only in improving process analysis and in optimizing process operating conditions, but also in the design of the control strategies for the process under consideration. A key problem, however, in the development of process models, either steady-state or dynamic, is parameter estimation. That is, since models of interest often include undetermined parameters, a reliable technique is needed for estimating these parameters from laboratory or process data so that a "best-fit" model is achieved.

In the standard approach to parameter estimation, a distinction is made between dependent and independent variables, with the assumption that there are no measurement errors in the independent variables. In chemical process modeling, however, parameters are often obtained by fitting experimental observations to models in which all variables are subject to error with a known or partly known variance. Thus, there is no distinction between dependent and independent variables. The error-in-variable (EIV) approach differs distinctly from the standard approach in that measurement errors in both dependent and independent system variables are taken into account when formulating the objective function in the parameter estimation problem. The best estimate of the parameters can then be obtained by minimizing the objective function subject to constraints representing the model equations. In many cases the constraints may be eliminated by substitution into the objective function. Thus, either a constrained or unconstrained optimization problem needs to be solved, which in general will be nonlinear and potentially nonconvex.

Since the optimization problem to be solved may be nonconvex, there may exist multiple local optima. However, the standard methods used to solve these problems are local methods that offer no guarantee that the global optimum, and thus the best set of model parameters, has been found. Hence, there is a need for global optimization in nonlinear parameter estimation. One approach that has been suggested is adaptive random search. Here the search for the optimal parameter values has a randomized component, allowing the potential for discovering multiple local optima. However, such stochastic methods cannot provide any mathematical guarantees that the global optimum has been found. Another approach, suggested by Esposito and Floudas (1998), is to reformulate the problem in terms of convex underestimating functions and then use a branch and bound procedure. This is a deterministic global optimization method that can provide a theoretical guarantee of global optimality. One difficulty with this approach is that in general it is necessary to perform problem reformulations and develop convex underestimators specific to each new application. Also, branch and bound methods implemented in floating point arithmetic may be vulnerable to rounding error problems, and thus lose their theoretical guarantees. An alternative approach for global optimization in this context is the use of interval analysis. Gau and Stadtherr (1999a, 2000) have successfully applied interval analysis in the estimation of parameters in the Wilson model for binary vapor-liquid equilibrium when using a standard (not EIV) relative least-squares approach. Not only did they discover the existence of multiple local minima in the relative least-squares objective function, but in several problems they also found new globally optimal parameter values that had been missed when a standard local optimizer was used (Gmehling et al., 1977).

We extend here the interval methodology to problems in process engineering in which the EIV approach to pa-

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rameter estimation is used. As examples, we consider the estimation of parameters in both steady- and unsteady-state models, including a vapor-liquid equilibrium (VLE) model, a CSTR model, and a reaction kinetics model. In each example, we demonstrate how a simple global optimization procedure based on interval analysis can be used to reliably and effectively determine the globally optimal parameter values, while simultaneously performing a data reconciliation. The method used involves the use of an interval-Newton technique combined with interval branch and bound. This method represents a deterministic approach to global optimization, and provides a mathematical and computational guarantee of global optimality in parameter estimation.

2 Error-in-Variable Approach

It should first be noted that several good introductions to the problem of parameter estimation are available (e.g, Bard, 1974). More details concerning the formulation of the error-in-variable approach are also available elsewhere (e.g., Kim et al., 1990; Esposito and Floudas, 1998).

Consider a model of the general functional form $\mathbf{f}(\boldsymbol{\theta}, \mathbf{z}) = \mathbf{0}$, where $\boldsymbol{\theta} = (\theta_1, \theta_2, \ldots, \theta_q)^{\mathrm{T}}$ is an unknown parameter vector for which the "best-fit" values are sought, $\mathbf{z}$ is the vector of state variables for the system to be modeled, and $\mathbf{f}$ is a vector of p model functions. Suppose that measurements $\mathbf{z}_i = (z_{i1}, ..., z_{in})^{\mathrm{T}}$ of state variables from $i = 1, \ldots, m$ experiments are available. Whether in laboratory experiments or process operations, it is impossible to measure the true values of state variables since all measurements are more or less subject to error. Thus there is a vector of measurement errors $\mathbf{e}_i = \tilde{\mathbf{z}}_i - \mathbf{z}_i$, $i = 1, \ldots, m$, that reflects the difference between the measured values $\mathbf{z}_i$ and the unknown "true" values $\tilde{\mathbf{z}}_i$. Using a maximum likelihood estimator and assuming that the errors $\mathbf{e}_i$ present a Gaussian distribution with zero mean and a known covariance matrix $\mathbf{V}$ that is constant over all experiments, then the objective in the parameter estimation problem is to minimize $\sum_{i=1}^{m} \mathbf{e}_i^{\mathrm{T}} \mathbf{V}^{-1} \mathbf{e}_i$. Since the covariance matrix is usually determined on the basis of the standard deviations in measuring the individual state variables, rather than in replicate measurements of the whole system, it is often assumed that the errors in each experiment are independent and uncorrelated. This means that $\mathbf{V}$ is a diagonal matrix, and each diagonal element v_{jj} can be chosen to be the square of standard deviation associated with the corresponding state variable; that is $v_{jj} = \sigma_j^2$. With these assumptions, the optimization problem becomes

$$\min_{\boldsymbol{\theta}, \tilde{\mathbf{z}}_i} \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{(\tilde{z}_{ij} - z_{ij})^2}{\sigma_j^2} \tag{1}$$

subject to the model constraints

$$\mathbf{f}(\boldsymbol{\theta}, \tilde{\mathbf{z}}_i) = \mathbf{0}, \quad i = 1, \ldots, m. \tag{2}$$

It should be noted that, since the optimization is over both $\boldsymbol{\theta}$ and $\tilde{\mathbf{z}}_i$, this is likely to be a nonlinear optimization problem even for models that are linear in the parameters.

This formulation of the parameter estimation problem is typically referred to as the error-in-variable (EIV) approach. The key distinction of this approach from classical least-squares (LS) regression is that in the EIV approach all variables are assumed to be subject to measurement errors, whereas in classical LS a distinction is made between dependent and independent variables, with the assumption that there are no measurement errors in the independent variables. Also note that, in solving the optimization problem above, the results not only provide an estimate of the parameter vector $\boldsymbol{\theta}$, but also an estimate of the "true" value of the state variable vector $\mathbf{z}$. Thus, in using the EIV approach, there is the advantage that both parameter estimation and data reconciliation problems are being solved simultaneously.

In the problems considered here, the p model equations can be used to solve algebraically for p of the n state variables. Thus, by substitution into the objective function in Eq. (1), an unconstrained optimization problem can be easily obtained. The unconstrained problem can be stated

$$\min_{\boldsymbol{\theta}, \tilde{\mathbf{v}}_i} \phi(\boldsymbol{\theta}, \tilde{\mathbf{v}}_i) \tag{3}$$

where $\tilde{\mathbf{v}}_i$, $i = 1, \ldots, m$, refers to the $n - p$ independent state variables not eliminated using the model equations, and $\phi(\boldsymbol{\theta}, \tilde{\mathbf{v}}_i)$ is the objective function in Eq. (1) after the p dependent state variables have been eliminated by substitution.

Use of the EIV approach in process systems engineering has attracted considerable attention, both in terms of specific practical applications and in terms of improving the numerical methods used to solve the optimization problem. Among the numerical issues that have been addressed are convergence difficulties, and the increased dimensionality of the problem, which unlike in classical LS, grows with the number of experiments. However, despite the fact that most EIV optimization problems are nonlinear, and many may be nonconvex, relatively little attention, with the notable exception of Esposito and Floudas (1998), has been given to the possible existence of multiple local minima, and thus the need for use of global optimization techniques. We will demonstrate here the use of interval analysis for solving the global optimization problems arising in parameter estimation by the EIV approach.

3 Interval Analysis

Several good introductions to interval analysis are available (e.g., Kearfott, 1996). Of particular interest here is the interval Newton technique. Given a nonlinear equation system with a finite number of real roots in some initial interval, this technique provides the capability to find (or, more precisely, narrowly enclose) all the roots of the system within the given initial interval. For the unconstrained minimization of the objective function in parameter estimation problems, a common approach is to seek stationary points, that is, to seek a solution of

$\mathbf{g}(\boldsymbol{\theta}, \tilde{\mathbf{v}}_i) \equiv \nabla\phi(\boldsymbol{\theta}, \tilde{\mathbf{v}}_i) = \mathbf{0}$. For simplicity, the vector of independent variables in this set of equations will be denoted $\mathbf{y} = (\boldsymbol{\theta}, \tilde{\mathbf{v}}_i)^{\mathrm{T}}$. The global minimum will be a root of this nonlinear equation system, but there may be many other roots as well, representing local minima and maxima and saddle points. Thus, for this approach to be reliable, the capability to find all the roots of $\mathbf{g}(\mathbf{y}) = \mathbf{0}$ is needed, and this is provided by the interval Newton technique. In practice, the interval Newton procedure can also be combined with an interval branch and bound technique, so that roots of $\mathbf{g}(\mathbf{y}) = \mathbf{0}$ that cannot be the global minimum need not be found.

The solution algorithm is applied to a sequence of intervals, beginning with some initial interval $\mathbf{Y}^{(0)}$ specified by the user. (In this section, upper case quantities are intervals, and lower case quantities real numbers.) This initial interval can be chosen to be sufficiently large to enclose all physically feasible behavior. It is assumed here that the global optimum will occur at an interior stationary minimum of $\phi(\mathbf{y})$ and not at the boundaries of $\mathbf{Y}^{(0)}$. Since the estimator ϕ is derived based on a product of Gaussian distribution functions corresponding to each data point, only a stationary global minimum is reasonable for statistical regression problems such as considered here. Details of the basic solution algorithm used are given by Gau and Stadtherr (2000). Only the key ideas of the methodology, together with a discussion of recent improvements, are presented here.

For an interval $\mathbf{Y}^{(k)}$ in the sequence, the first step in the solution algorithm is the *function range test*. Here an *interval extension* $\mathbf{G}(\mathbf{Y}^{(k)})$ of the function $\mathbf{g}(\mathbf{y})$ is calculated. An interval extension provides upper and lower bounds on the range of values that a function may have in a given interval. It is often computed by substituting the given interval into the function and then evaluating the function using interval arithmetic. The interval extension so determined is often wider than the actual range of function values, but it always includes the actual range. If there is any component of the interval extension $\mathbf{G}(\mathbf{Y}^{(k)})$ that does not contain zero, then we may discard the current interval $\mathbf{Y}^{(k)}$, since the range of the function does not include zero anywhere in this interval, and thus no solution of $\mathbf{g}(\mathbf{y}) = \mathbf{0}$ exists in this interval. We may then proceed to consider the next interval in the sequence, since the current interval cannot contain a stationary point of $\phi(\mathbf{y})$. Otherwise, if $\mathbf{0} \in \mathbf{G}(\mathbf{Y}^{(k)})$, then testing of $\mathbf{Y}^{(k)}$ continues.

The next step is the *objective range test*. The interval extension $\Phi(\mathbf{Y}^{(k)})$, which contains the range of $\phi(\mathbf{y})$ over $\mathbf{Y}^{(k)}$, is computed. If the lower bound of $\Phi(\mathbf{Y}^{(k)})$ is greater than a known upper bound on the global minimum of $\phi(\mathbf{y})$, then $\mathbf{Y}^{(k)}$ cannot contain the global minimum and need not be further tested. Otherwise, testing of $\mathbf{Y}^{(k)}$ continues.

The next step is the interval Newton test. Here the linear interval equation system

$$G'(\mathbf{Y}^{(k)})(\mathbf{N}^{(k)} - \mathbf{y}^{(k)}) = -\mathbf{g}(\mathbf{y}^{(k)}) \qquad (4)$$

is set up and solved for a new interval $\mathbf{N}^{(k)}$, where $G'(\mathbf{Y}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{g}(\mathbf{y})$, and $\mathbf{y}^{(k)}$ is a point in the interior of $\mathbf{Y}^{(k)}$, usually taken to be the midpoint. Comparison of the current interval $\mathbf{Y}^{(k)}$ and the *image* $\mathbf{N}^{(k)}$ provides a powerful existence and uniqueness test (Kearfott, 1996). If $\mathbf{N}^{(k)}$ and $\mathbf{Y}^{(k)}$ have a null intersection, then this is mathematical proof that there is no solution of $\mathbf{g}(\mathbf{y}) = \mathbf{0}$ in $\mathbf{Y}^{(k)}$. If $\mathbf{N}^{(k)}$ is a proper subset of $\mathbf{Y}^{(k)}$, then this is mathematical proof that there is a *unique* solution of $\mathbf{g}(\mathbf{y}) = \mathbf{0}$ in $\mathbf{Y}^{(k)}$. If neither of these two conditions is true, then no conclusions can be made about the number of solutions in the current interval. However, it is known (Kearfott, 1996) that any solutions that do exist must lie in the intersection of $\mathbf{N}^{(k)}$ and $\mathbf{Y}^{(k)}$. If this intersection is sufficiently smaller than the current interval, one can proceed by reapplying the interval Newton test to the intersection. Otherwise, the intersection is bisected, and the resulting two intervals added to the sequence of intervals to be tested. These are the basic ideas of an interval Newton/generalized bisection (IN/GB) method. When properly implemented, this method provides a procedure that is mathematically *and* computationally guaranteed to find the global minimum of $\phi(\mathbf{y})$, or, if desired (by turning off the objective range test), to enclose *all* of its stationary points.

Two recent improvements in the basic methodology have also been incorporated into the implementation of IN/GB used here. The first of these involves the method used to solve Eq. (4) for the image $\mathbf{N}^{(k)}$. The standard method used is a preconditioned Gauss-Seidel approach in which an inverse midpoint preconditioning matrix is used (this is either the inverse of the midpoint matrix of the interval Jacobian $G'(\mathbf{Y}^{(k)})$ or the inverse of the point Jacobian matrix evaluated at the midpoint $\mathbf{y}^{(k)}$). However, by using a different preconditioning scheme it may be possible to more tightly bound the solution set of Eq. (4) and thus obtain a smaller interval for the image, which will in general improve the efficiency of the interval Newton step in reducing or eliminating intervals under consideration. With this in mind, we have recently developed (Gau and Stadtherr, 1999b) a new hybrid preconditioning scheme which incorporates the standard inverse midpoint scheme with a new approach in which preconditioning rows are generated on a row by row basis in order to optimize the result of the interval Newton step. Details of this preconditioning procedure are beyond the scope of this paper and will be provided elsewhere. The second improvement in the basic methodology involves the formulation of Eq. (4). Here the real point $\mathbf{y}^{(k)}$ can be any point in the interval $\mathbf{Y}^{(k)}$, but is most commonly chosen to be the midpoint of $\mathbf{Y}^{(k)}$. We have developed a new procedure in which this real point is allowed to be varied in order to optimize the result of the interval Newton step. As in the case of the hybrid preconditioning scheme, this can be done on a row-wise (coordinate-wise) basis. Again, details of this procedure are beyond the scope of this paper and will be presented elsewhere. For problems with more

than a small number of independent variables, such as the example problems considered below, which range in size from 12 to 32 variables, use of these improvements in the methodology is essential to obtain efficient computational performance.

4 Examples and Results

4.1 Problem 1: Vapor-Liquid Equilibrium (VLE) Model

Because of its importance in the design of separation systems, much attention has been given to modeling the thermodynamics of phase equilibrium in fluid mixtures. Typically these models take the form of excess Gibbs energy or activity coefficient models or equation of state models, with binary parameters in the models determined by parameter estimation from experimental data.

As an example, we consider here the EIV estimation from binary VLE data of the two parameters in the Van Laar equation for liquid-phase activity coefficient. This problem has also been considered by Kim et al. (1990) and Esposito and Floudas (1998). The binary mixture of interest is the system methanol(1) and 1,2-dichloroethane(2). The experimental data consist of five experimental data points for four measured state variables: pressure P (mmHg), temperature T (K), liquid mole fraction x_1 of component 1, and vapor mole fraction y_1 of component 1.

The model equations to describe this system are expressed here as

$$P = \gamma_1 x_1 p_1^0(T) + \gamma_2 (1 - x_1) p_2^0(T) \tag{5}$$

$$y_1 = \frac{\gamma_1 x_1 p_1^0(T)}{\gamma_1 x_1 p_1^0(T) + \gamma_2 (1 - x_1) p_2^0(T)} \tag{6}$$

where (using the data in Esposito and Floudas, 1998)

$$p_1^0(T) = \exp\left[18.5875 - \frac{3626.55}{T - 34.29}\right]$$

$$p_2^0(T) = \exp\left[16.1764 - \frac{2927.17}{T - 50.22}\right]$$

and from the Van Laar equation

$$\gamma_1 = \exp\left[\frac{A}{RT}\left(1 + \frac{A}{B}\frac{x_1}{1 - x_1}\right)^{-2}\right]$$

$$\gamma_2 = \exp\left[\frac{B}{RT}\left(1 + \frac{B}{A}\frac{1 - x_1}{x_1}\right)^{-2}\right] .$$

Again following Esposito and Floudas (1998), temperature is scaled by a reference temperature, $T_\mathrm{r} = 323.15$ K. In these terms, the parameter vector is $\boldsymbol{\theta} = (\frac{A}{RT_\mathrm{r}}, \frac{B}{RT_\mathrm{r}})^\mathrm{T}$ and the state variable vector is $\mathbf{z} = (x_1, T', P, y_1)^\mathrm{T}$ where $T' = T/T_\mathrm{r}$. The standard deviations (using the data in Esposito and Floudas, 1998) in the measurement of $\mathbf{z}$ are $\boldsymbol{\sigma} = (0.005, 3.09 \times 10^{-4}, 0.75, 0.015)^\mathrm{T}$.

In order to formulate the EIV parameter estimation problem as an unconstrained optimization problem, the model equations (5) and (6) are used to eliminate P and y_1. Thus, the vector of independent state variables is $\mathbf{v} = (x_1, T')^\mathrm{T}$. In the optimization problem the independent variables are $\boldsymbol{\theta}$ (two variables) and $\tilde{\mathbf{v}}_i$, $i = 1, \ldots, 5$ (five vectors of two variables each), for a total of 12 independent variables. The initial intervals on the parameters θ_1 and θ_2 were both taken as $[1, 2]$ (as in Esposito and Floudas, 1998). In order to give the initial interval a statistical 99.7% probability of containing the true state variable values, the initial intervals on the state variables were taken as $\tilde{x}_{1,i} \in [x_{1,i} - 3\sigma_1, x_{1,i} + 3\sigma_1]$ and $\tilde{T}_i' \in [T_i' - 3\sigma_2, T_i' + 3\sigma_2]$ for $i = 1, \ldots, 5$.

Using the interval methodology described above, the globally optimal parameter values obtained were $\theta_1 = 1.9116$ and $\theta_2 = 1.6083$, with an objective value of 3.32582. It should be noted that, while point approximations are reported here, and in subsequent examples, for the parameter estimation results, we have actually determined verified enclosures of the corresponding stationary points. Each such enclosure is an extremely narrow interval known to contain a *unique* stationary point, based on the interval-Newton uniqueness test described above. By turning off the objective range test, thus allowing the technique to enclose *all* the stationary points, not just the global minimum, it was also ascertained that there is only one stationary point (the global minimum) in the specfied initial interval.

The CPU time required to perform the global parameter estimation was 807.9 seconds on a Sun Ultra 2/1300 workstation. This is roughly half the CPU time required by Esposito and Floudas (1998) to obtain these results on an HP 9000 C160 machine (which, based on the SPECfp95 benchmark, is a slightly faster machine than the Sun Ultra 2/1300).

4.2 Problem 2: CSTR Model

This example considers an adiabatic CSTR with an irreversible, first-order reaction

$$A \xrightarrow{\mathrm{k_1}} B$$

as discussed by Kim et al. (1990) and Esposito and Floudas (1998). As discussed in more detail below, simulated measurements with noise added were created for five quantities: the inlet temperature T_0 (K), the outlet temperature T (K), the outlet concentrations of A and B, denoted A and B (mol/L), respectively, and the inlet concentration A_0 (mol/L) of A.

With the assumption that the feed is pure A, the model for the irreversible reaction system is

$$\frac{1}{\tau}(A_0 - A) - k_1 A = 0 \tag{7}$$

$$\frac{-B}{\tau} + k_1 A = 0 \tag{8}$$

$$\frac{1}{\tau}(T_o - T) + \frac{-\Delta H_\mathrm{r}}{\rho C_\mathrm{p}}(k_1 A) = 0 \tag{9}$$

where τ = 100 s is the residence time of reactor, ΔH_{r} = -4180 J/mol is the heat of reaction, ρ = 1.0 g/L is the density of the reaction mixture, and C_{p} = 4.18 J/g K is the heat capacity of the reaction mixture. The reaction rate constant can be expressed as

$$k_1 = c_1 \exp\left(\frac{-Q_1}{RT}\right)$$

where the Arrhenius constants c_1 and Q_1 are the parameters to be determined. Next a parameter transformation is done, similar to that used by Kim et al. (1990) and Esposito and Floudas (1998), resulting in

$$k_1' = \frac{1}{k_1} = \theta_1 \exp\left[-\theta_2\left(\frac{T_{\mathrm{r}}}{T} - 1\right)\right]$$

with

$$\theta_1 = \frac{1}{c_1}\exp\left(\frac{Q_1}{RT_{\mathrm{r}}}\right)$$

$$\theta_2 = \frac{-Q_1}{RT_{\mathrm{r}}}$$

where T_{r} is some reference temperature. The parameter vector is thus the vector $\boldsymbol{\theta} = (\theta_1, \theta_2)^{\mathrm{T}}$, whose components are given by the above expressions. Ten simulated data points for $\mathbf{z} = (A_0, A, B, T_0, T)^{\mathrm{T}}$ were taken from Esposito and Floudas (1998). These simulated data were created using c_1 = 5000 s^{-1} and $Q_1 = 83600$ J/mol with added noise having a standard deviation of $\boldsymbol{\sigma} = (0.01, 0.01, 0.01, 1.0, 1.0)^{\mathrm{T}}$.

To formulate the EIV parameter estimation problem as an unconstrained optimization problem, the model equations (7–9) are used to eliminate A_0, A and T_0. Thus, the vector of independent state variables is $\mathbf{v} = (B, T)^{\mathrm{T}}$. In the optimization problem the independent variables are $\boldsymbol{\theta}$ (two variables) and $\tilde{\mathbf{v}}_i$, $i = 1, \ldots, 10$ (ten vectors of two variables each), for a total of 22 independent variables. For the reference temperature T_{r}, a value of 680 K, which is within the range of the measured temperature values (663–754 K), was chosen. The initial intervals used for the parameters were $\theta_1 \in [24.165, 141124.8]$ s and $\theta_2 \in [-17.65, -5.88]$; these were chosen to correspond to the initial intervals used by Esposito and Floudas (1998), who use a different T_{r} (800 K) and a slightly different parameter transformation. As done in the previous example, in order to give the initial interval a statistical 99.7% probability of containing the true state variable values, the initial intervals on the state variables were taken as $\tilde{B}_i \in [B_i - 3\sigma_3, B_i + 3\sigma_3]$ and $\tilde{T}_i \in [T_i - 3\sigma_5, T_i + 3\sigma_5]$ for $i = 1, \ldots, 10$.

Using the interval methodology, the results obtained for the globally optimal parameter values were $\theta_1 = 532.476$ s and $\theta_2 = -14.627$, corresponding to an objective function value of 29.04731. In terms of the original parameters, the results are $c_1 = 4229.0389\ \mathrm{s}^{-1}$ and $Q_1 = 82695.5491$ J/mol. By running the algorithm with the objective range test turned off, it was demonstrated that this global minimum is the only stationary point in the specified initial interval.

The CPU time required for the 22-variable global optimization was 28.8 seconds on a Sun Ultra 2/1300 workstation. As in the previous example, this time compares very favorably with that reported by Esposito and Floudas (1998), who tried three different problem formulations, with a fastest solution time of 282.2 seconds on an HP 9000 C160, which, as noted above, is a slightly faster machine than the Sun Ultra 2/1300. Thus, an order of magnitude improvement in computation time is observed.

4.3 Problem 3: Batch Reaction Kinetics Model

This example considers the chemical conversion of initially pure species A to species B in an isothermal batch reactor

$$A \xrightarrow{\mathrm{k}} B$$

a problem originally presented by Bard (1974). Experimental measurements were made of the reaction time t (h), the system temperature T (K), and the fraction y of the initial amount of component A that remains at time t.

This system is modeled by the the differential equation

$$\frac{dy}{dt} = -ky$$

where k is a first-order rate constant. With the initial condition $y = 1$ at $t = 0$, the solution to this equation is

$$y = \exp(-kt) \tag{10}$$

where the reaction rate constant k can be expressed as

$$k = \theta_1 \exp\left(-\frac{\theta_2}{T}\right).$$

Here the Arrhenius constants θ_1 and θ_2 are the parameters to be estimated using the EIV approach. The first data set to be considered is taken from Table 5-2 (Sections 5-21 and 6-13) in Bard (1974), and consists of 15 data points, five at each of three different temperatures (100 K, 200 K and 300 K). Based on calculations done by Bard (1974), the vector of standard deviations was set as $\boldsymbol{\sigma} = (0.01, 0.5, 0.016624)^{\mathrm{T}}$ for the measurement vector $\mathbf{z} = (t, T, y)^{\mathrm{T}}$.

To obtain an unconstrained optimization problem, the model equation (10) was used to eliminate y. Thus, the vector of independent state variables is $\mathbf{v} = (t, T)^{\mathrm{T}}$. In the optimization problem the independent variables are $\boldsymbol{\theta}$ (two variables) and $\tilde{\mathbf{v}}_i$, $i = 1, \ldots, 15$ (15 vectors of two variables each), for a total of 32 independent variables. The initial intervals on the parameters were set at $\theta_1 \in [1, 10000]\ \mathrm{h}^{-1}$ and $\theta_2 \in [1, 10000]$ K. The initial intervals on the state variables were again set using plus and minus three standard deviations; that is, $\tilde{t}_i \in [t_i - 3\sigma_1, t_i + 3\sigma_1]$ and $\tilde{T}_i \in [T_i - 3\sigma_2, T_i + 3\sigma_2]$ for $i = 1, \ldots, 15$.

The results of applying the interval method for global optimization are the parameter values $\theta_1 = 1171.817\ \mathrm{h}^{-1}$ and $\theta_2 = 1027.954$ K with the globally minimum objective value of 16.55240. The CPU time required for the

32-variable global optimization problem was 1317.8 seconds on a Sun Ultra 2/1300 workstation.

A second data set was also considered for this system. This data set involves seven data points, the first five of which (at 100 K) are the same as in the first data set. The sixth and seventh data points are at $T_6 = T_7 = 200$ K and are $y_6 = 0.554$ at $t_6 = 0.07$ h and $y_7 = 0.669$ at $t_7 = 0.16$ h. Because of suspicions about the quality of the data at $T = 200$ K, for this case the initial intervals on $\tilde{t}_i$ and $\tilde{T}_i$, $i = 1, \ldots, 7$, were set using plus and minus five standard deviations. This is a 16-variable optimization problem. The globally optimal parameter values found for this case are $\theta_1 = 336.474$ h^{-1} and $\theta_2 = 870.757$ K, with an objective value of 34.24904. The CPU time required was 100.5 seconds on a Sun Ultra 2/1300 workstation.

In order to investigate the possibility of other local, but not global, minima for this problem, the problem was resolved with the objective range test turned off. This means that the interval method will find *all* the stationary points within the specified initial interval, not just the global minimum. When this was done, two stationary points were found, one the global minimum reported above, and the second a local minimum at $\theta_1 = 7575.339$ h^{-1} and $\theta_2 = 1494.218$ K, with the objective value of 36.46666. Even though the objective function values at these two stationary points do not differ greatly, there are substantial differences in predicted reaction rates $r = ky$. For example, with the globally optimal parameter values, the initial reaction rate at 100 K is 0.0556 h^{-1}. However, if the parameter values that are only locally optimal are used, the predicted initial reaction rate at 100 K is 0.0025 h^{-1}, over an order of magnitude different from the predicted result using the globally optimal parameters. Clearly, if a local optimizer was used on this problem, and it converged to the local, but not global, solution, and those results were used for reactor design studies, the results could be dangerously incorrect.

Since, as noted above, there is some suspicion about the quality of this data set, the data reconciliation results (i.e., the components of the measurement errors $\tilde{\mathbf{z}}_i - \mathbf{z}_i$, $i = 1, \ldots, 7$) are also of interest. The relatively large errors that can be observed, based on either the globally or locally optimal solution, for data points $i = 6$ and $i = 7$ (i.e., the data at 200 K), is a strong indication that these two points are outliers, perhaps due to an instrumentation failure, or other systematic error.

It is interesting to also consider the case in which these two "bad" data points are replaced by "good" data, in this case the first two data points at 200 K from the first data set. Now, when the 16-variable global optimization is done, the parameter values found are $\theta_1 = 856.410$ h^{-1} and $\theta_2 = 961.505$ K. These yield a predicted initial reaction rate at 100 K of 0.0571 h^{-1}, quite close to that predicted using the globally optimal result from the "bad" data set.

5 Concluding Remarks

We have demonstrated here a new methodology for reliably solving nonlinear parameter estimation problems using the EIV approach in chemical process modeling. The method is based on interval analysis, in particular an interval Newton/generalized bisection algorithm. The approach provides a mathematical and computational guarantee that the global optimum in the parameter estimation problem is found. The technique used is general-purpose and was applied here to a diverse set of applications. The computation times required are significantly less than those reported for a convex underestimation approach to the global optimization, but are still much larger than what is required by the local optimization methods typically used in parameter estimation. Of course, such local methods give no guarantee that the global optimum will be found, and as demonstrated in the batch reaction kinetics example, results that are only locally optimal could lead to extremely poor modeling results. Thus, there is a choice between fast methods that may give the wrong answer, or slower methods that are guaranteed to give the correct answer. Ultimately, the modeler must make a decision concerning how important it is to get the correct answer.

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