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ERROR ANALYSIS OF VAPOR
PRESSURE MEASUREMENTS

Aivars K. R. Celminš

January 1984



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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I. INTRODUCTION

The relation between vapor pressure and temperature can be approximated for certain chemical compounds by the so-called Antoine equation, viz.,

$$\lg(p/p_R) - A + B/[(T - 273.15) + C] = 0 \quad , \quad (1.1)$$

where p (Pa) is the vapor pressure, p_R (Pa) is a reference pressure (usually $p_R = 1 \text{ torr} = 7.50064 \cdot 10^{-3} \text{ Pa}$), T (K) is temperature, and A , B and C are model parameters. The latter are determined for a particular compound by data fitting to observed p, T -correspondences. If this is done by a simple least squares method, then it is customary and also advantageous numerically to consider as observations the quantities $\lg(p/p_R)$ instead of the actually observed pressures.^{1,2} Penski and Latour² point out, however, that such a treatment of pressure data implies the assumption that inaccuracies of the pressure observations are proportional to the observed pressures. Also implied by the published treatments of vapor pressure data is that inaccuracies of temperature observations can be neglected. The adequacy of these two assumptions has not been discussed in the literature, but, because they do influence the model fitting results, it is important to have some means by which these or other assumptions about data accuracy can be tested. A test can be provided, for instance, by analyzing the different sets of residuals that are obtained with different assumptions about measurement errors. Based on such analyses one then may choose an optimal error model according to some criterion or even develop an algorithm that produces the optimal model automatically. Similar problems have been discussed by Cohen^{3,4} and Nielsen.⁵ Both authors suggest iterative algorithms for the determination of optimal error models. In this report, the approach of Nielsen is

¹Herbert R. Kemme and Saul I. Kreps, "Vapor Pressure of Primary *n*-Alkyl Chlorides and Alcohols," *Journal of Chemical and Engineering Data*, Vol. 14, pp. 98-102, 1969.

²Elwin C. Penski and Leo J. Latour, "Conversational Computation Method for Fitting the Antoine Equation to Vapor Pressure-Temperature Data," Edgewood Arsenal Technical Report EATR 4491, February 1971 (AD 881829L).

³E. Richard Cohen, "'Extended' Least Squares," Rockwell International Science Center Report SCTR-76-1, January 1976.

⁴E. Richard Cohen, "An Extended Least Squares Algorithm for Treating Inconsistent Data," Rockwell International Science Center Report SCTR-78-11, December 1978.

⁵Kurt Nielsen, "A Method for Optimizing Relative Weights in Least Squares Analysis," *Acta Crystallographica*, A33, pp. 1009-1010, 1977.

generalized so that it can be applied to a wider class of data fitting problems, including vapor pressure measurements. Tests of the method on typical vapor pressure data indicate, however, that an automatic determination of error parameters as suggested by Nielsen is not feasible for this type of data. More appropriate is an interactive computation, whereby the user determines the optimal parameters based on the results of the analyses of residuals.

In Section II we describe the generalized formulation of Nielsen's approach and the suggested variation of it. Residual analysis is treated in Section III, and Sections IV and V contain test results with simulated and real data, respectively.

II. SIMULTANEOUS FITTING OF PRESSURE MODELS AND ERROR MODELS

An iterative process for the simultaneous determination of event model parameters and error model parameters has been suggested by Nielsen.⁵ His problem formulation is, however, restricted to weighted least squares adjustments and, consequently, to single component observations. In this section, the problem is reformulated so that general least squares model fitting can be treated, including cases with multiple component observations and models that are formulated by sets of simultaneous equations. The generalization is needed for the treatment of vapor pressure data because they consist of observation vectors with two components, pressure and temperature, each of which may be subject to errors and adjustment.

Let the general least squares model fitting task be formulated as the following constrained minimization problem:

$$\begin{aligned} \underset{c, t}{\text{minimize}} \quad W(c, t) &= \sum_{i=1}^s c_i^T R_i^{-1} c_i, \\ \text{subject to} \quad F_i(X_i + c_i; t) &= 0, \quad i=1, \dots, s, \end{aligned} \quad (2.1)$$

where X_i are the observations (observed vectors), c_i are corresponding residuals, R_i are estimated variance-covariance matrices of the components of X_i , t is a model parameter vector, and $F_i(X_i; t) = 0$ are model equations.

In general, the model equations are sets of simultaneous equations; i.e., the F_i are vector functions. In the case of vapor pressure measurements, the model equations are scalar equations representing some form of the Antoine Eq. (1.1). We shall give the specific formulations of the model fitting and error fitting for vapor pressure measurements at the end of this section.

The solution of the problem (2.1) consists of the set c of the residuals c_i and a corresponding model parameter vector t . The given input consists of the observations X_i and the estimated variance-covariance matrices R_i (in addition to the given functions F_i). Our goal is to find a set of R_i that is optimal in some sense. To that end we assume that the R_i are expressed as

functions of the X_i , c_i , the model parameter vector t , and a free error parameter vector θ . This reduces the problem of finding s optimal matrices R_i to the determination of a single optimal error parameter vector θ .

Next, we introduce a function S as a measure for the optimality of the set of the variance-covariance matrices R_i by the following definition:

$$S = 1 + \frac{1}{\ln s} \sum_{i=1}^s q_i \ln q_i, \quad (2.2)$$

where

$$q_i = c_i^T R_i^{-1} c_i / \sum_{j=1}^s c_j^T R_j^{-1} c_j. \quad (2.3)$$

Our goal is to find such a set of $R_i(\theta)$ that produces a minimum value for S . The corresponding error parameter θ we call the optimal parameter.

The definition of S by Eq. (2.2) as an objective function was suggested by Nielsen⁵ and based on the following properties of S :

- (a) S is a maximum and equals one if all but one of the q_i are zero.
- (b) S is a minimum and equals zero if all $q_i = 1/s$.
- (c) Any averaging of the q_i reduces S ; that is, if

$$0 \leq a_{ij} \leq 1,$$

$$\sum_{j=1}^s a_{ij} = \sum_{i=1}^s a_{ij} = 1 \quad \text{for } i, j = 1, \dots, s$$

and

$$q_i^* = \sum_{j=1}^s a_{ij} q_j,$$

then

$$S(q^*) \leq S(q).$$

Hence, a minimization of S tends to equalize the q_i . The numerator in the definition (2.3) of q_i can be considered as the square of a norm of the residual c_i . Therefore, an equalization of the q_i means an equalization of the norms of the residuals. Cohen³ points out that one can also use instead of this S other objective functions with similar properties. In limited numerical experiments with such functions and vapor pressure data we did not find objective functions that would offer numerical or other advantages over S . The remaining considerations in this report are, therefore, limited to the objective function S as defined by Eq. (2.2).

Nielsen suggests an automatic determination of the error parameter θ concurrently with a solution of the least squares problem by the following iteration procedure:

Step 1. Choose an initial error parameter vector θ .

Step 2. Solve the least squares problem (2.1).

Step 3. Find a new error parameter vector Θ by solving the minimization problem

$$\underset{\theta}{\text{minimize}} \quad S(c, R(\theta)) \quad .$$

Step 4. Replace θ by Θ and repeat the procedure starting with Step 2.

An essential part of the algorithm is Step 3 at which S is minimized by varying the $R_i(\theta)$ while keeping the residuals c_i fixed. The minimization can be achieved quite effectively by a simplex method because usually the number of components of θ is relatively small (less than ten). Nielsen did not investigate the convergence properties of the algorithm but reports convergence in two steps when the algorithm was applied to a data set with 882 observations. At the end of the iterations Nielsen compared the distribution of the (weighted) residuals with normal distribution and found good agreement.

The minimization of S at Step 3 of the algorithm is also a weak point of the method because it prevents the algorithm from producing the optimal θ exactly, although the algorithm may produce a good approximation. In order to show this, let us assume that the minimum of S is determined by setting its derivative with respect to θ equal to zero (instead of using a simplex method). The residuals c_i which appear in the definition (2.2) and (2.3) of S are functions of θ , because they are determined at Step 2 from a least squares fit in which the $R_i(\theta)$ are used as input. Therefore, the formal derivative of S with respect to θ can be symbolically expressed by

$$\frac{dS}{d\theta} = \frac{\partial S}{\partial c} \frac{\partial c}{\partial R} \frac{dR}{d\theta} + \frac{\partial S}{\partial R} \frac{dR}{d\theta} \quad . \quad (2.4)$$

A minimum of S and the corresponding $\theta = \theta$ can be obtained by solving the equation $dS/d\theta = 0$. However, at Step 3 of the algorithm one seeks the minimum of S with respect to θ for fixed c . This is equivalent to solving the equation

$$\frac{\partial S}{\partial R} \frac{dR}{d\theta} = 0 \quad . \quad (2.5)$$

The solution of Eq. (2.5) may be a good approximation to the solution of the complete equation $dS/d\theta = 0$, if the first term on the right-hand side of Eq. (2.4) is small. However, by setting only the second term equal to zero one never obtains the exact solution because the first term always dominates when the second term approaches zero. (We are not interested in the limiting solution $dR/d\theta = 0$.) On the other hand, if the first term is large, then its neglect can prevent the algorithm from converging even to an approximate value of the optimal θ . Experiments with vapor pressure data, indeed, have shown that failure to converge or a convergence to obviously wrong values of θ do occur. Therefore, we recommend determination of the minimum of S by direct search, e.g., by plotting S as a function of θ instead of using the outlined Nielsen's algorithm. We shall illustrate the behavior of $S(\theta)$ with some examples in Sections IV and V.

Next, we specialize the general formulation of the problem to vapor pressure data. The data vectors are

$$X_i = \begin{pmatrix} p_i \\ T_i \end{pmatrix} , \quad i = 1, \dots, s \quad , \quad (2.6)$$

the residual vectors are

$$c_i = \begin{pmatrix} c_{pi} \\ c_{Ti} \end{pmatrix} , \quad i = 1, \dots, s \quad (2.7)$$

and the constraint equations are, e.g.,

$$\lg [(p_i + c_{pi})/p_R] - A + B/(T_i + c_{Ti} - 273.15 + C) = 0 \quad , \quad i = 1, \dots, s \quad , \quad (2.8a)$$

or

$$(p_i + c_{pi})/p_R - 10^{A - B/(T_i + c_{Ti} - 273.15 + C)} = 0 \quad , \quad i = 1, \dots, s \quad . \quad (2.8b)$$

We consider the following models for the standard errors of pressure and temperature, respectively,

$$\left. \begin{aligned} e_{pi}/p_R &= e_o [1 + \theta_1 (p_i + c_{pi})/p_R] , \\ e_{Ti} &= e_o \theta_2 , \end{aligned} \right\} \quad i = 1, \dots, s \quad (2.9)$$

where e_o is the standard error of weight one. It is defined in terms of the least squares objective function W by

$$e_o = \sqrt{W/(s-3)} , \quad (2.10)$$

because the Antoine model equation has three free parameters. The error parameter θ has according to this definition two components. The models of the variance-covariance matrices R_i we define by

$$R_i = \begin{pmatrix} p_R^2 & [1 + \theta_1 (p_i + c_{pi})/p_R]^2 & 0 \\ 0 & \theta_2^2 \end{pmatrix} . \quad (2.11)$$

The least squares objective function is, therefore,

$$W = \sum_{i=1}^s \left[\left(\frac{c_{pi}/p_R}{1 + \theta_1 (p_i + c_{pi})/p_R} \right)^2 + \left(\frac{c_{Ti}}{\theta_2} \right)^2 \right] . \quad (2.12)$$

The quantities q_i that enter the definition (2.2) of S are

$$q_i = \left[\left(\frac{c_{pi}/p_R}{1 + \theta_1 (p_i + c_{pi})/p_R} \right)^2 + \left(\frac{c_{Ti}}{\theta_2} \right)^2 \right] / W \quad (2.13)$$

The error models (2.9) were chosen by the following considerations. The pressure standard error e_{pi} is constant if θ_1 is small and it approaches a constant relative error if θ_1 is large. Hence, by permitting θ_1 to vary we should be able to determine whether a constant or a relative pressure standard error is more appropriate. The temperature standard error is likely to be constant and, therefore, the corresponding model for e_{Ti} does not include a term proportional to the temperature. By setting the parameter $\theta_2 = 0$ we obtain with this model also the special case in which the temperature errors are neglected.

III. REDUCED RESIDUALS

One measure for the goodness of the solution of the problem described in Section II is the final value of the objective function S . Nielsen suggests as another measure an investigation of the distribution of weighted residuals and a comparison of the distribution with a normal distribution. The suggestion is easy to implement if the observations and residuals are scalars. In the general formulation (2.1) of the adjustment problem, however, the observables are not necessarily scalars and, therefore, one has to deal with multidimensional distributions of measurement errors and residuals. On the other hand, the effective dimensionality of the residuals is not necessarily the same as that of the measurement errors because it is reduced by the constraint equations $F_i(X_i + c_i; t) = 0$ that must be satisfied by the residuals. For instance, if one is fitting a straight line to observations of x and y , and the R_i are unit matrices, then the measurement error distribution is two-dimensional, but all residuals have the same direction (orthogonal to the line); that is, they span only a one-dimensional residual space. For this reason, an investigation of residual distributions should be sensibly done in spaces that have appropriately reduced dimensions. Quantities with the proper dimensionality are the reduced residuals a_i which we define by

$$a_i = (F_{xi} R_i F_{xi}^T)^{-1/2} F_{xi} c_i, \quad (3.1)$$

where

$$F_{xi} = \frac{\partial F_i(X_i + c_i; t)}{\partial X_i} \quad (3.2)$$

are the Jacobian matrices of the model functions. The dimension of a_i equals the dimension of the constraint function F_i . If the constraint is scalar, as in a fitting of a $(n-1)$ -dimensional hypersurface in a n -dimensional space, then the reduced residuals a_i are scalars. The components of the reduced residuals are dimensionless, in contrast to the components of the least squares residuals c_i which in general have different physical dimensions (pressure and temperature in case of vapor pressure measurements).

Further relations between the a_i and c_i can be derived from the equation

$$c_i = R_i F_{xi}^T (F_{xi} R_i F_{xi}^T)^{-1} F_{xi} c_i \quad (3.3)$$

that is exactly satisfied by least squares residuals.⁶ Eqs. (3.1) and (3.3) imply

$$c_i = R_i F_{xi}^T (F_{xi} R_i F_{xi}^T)^{-1/2} a_i \quad (3.4)$$

and

$$c_i^T R_i^{-1} c_i = a_i^T a_i \quad (3.5)$$

A reasonable measure of the size of the residual c_i is the elliptic norm

$$||c_i|| = (c_i^T R_i^{-1} c_i)^{1/2} \quad (3.6)$$

Eq. (3.5) shows that the Euclidean norm of the reduced residual a_i equals the elliptic norm (3.6) of the least squares residual c_i .

In the special case with scalar constraints $F_i = 0$, the definition (3.1) of the reduced residuals a_i simplifies to

$$a_i = (c_i^T R_i^{-1} c_i)^{1/2} \text{sgn}(F_{xi} c_i) \quad (3.7)$$

In an elementary least squares curve fitting problem where the observables are one-dimensional and the constraints have the special form $X_i + c_i - f_i(t) = 0$, the definition (3.7) further simplifies to

$$a_i = c_i / e_i = c_i \sqrt{w_i} \quad (3.8)$$

where e_i is the estimated standard error of the observation X_i and w_i is the weight of the observation to be used for a weighted least squares adjustment. Hence, in such problems, the reduced residuals (3.1) are identical to the usual weighted residuals.

⁶Aivars Celmiņš, "Least Squares Adjustment with Finite Residuals for Non-Linear Constraints and Partially Correlated Data," US Army Ballistic Research Laboratory Report BRL R 1658, July 1973 (AD 766283).

Next, we consider relations between the reduced residuals and observational errors. Let $\bar{t}$ be the true value of the model parameter and let $\bar{c}_i$ be the true residuals (negative errors) of the observations X_i . Then by definition

$$F_i(X_i + \bar{c}_i; \bar{t}) = 0 \quad . \quad (3.9)$$

Expanding Eq. (3.9) at the least squares position $(X_i + c_i; t)$ and only keeping the linear terms of the expansion, one obtains

$$F_i(X_i + c_i; t) + F_{xi} \cdot (\bar{c}_i - c_i) + F_{ti} \cdot (\bar{t} - t) = 0 \quad , \quad (3.10)$$

where

$$F_{ti} = \frac{\partial F_i(X_i + c_i; t)}{\partial t} \quad (3.11)$$

and F_{xi} is defined by Eq. (3.2). The first term in Eq. (3.10) vanishes because c_i and t are solutions of the least squares problem (2.1). Therefore, one has the following relation between c_i and $\bar{c}_i$ (neglecting higher order terms of $\bar{c}_i - c_i$ and $\bar{t} - t$)

$$F_{xi} c_i = F_{xi} \bar{c}_i - F_{ti} \cdot (\bar{t} - t) \quad . \quad (3.12)$$

Defining reduced errors $\bar{a}_i$ in the same fashion as the reduced residuals by

$$\bar{a}_i = (F_{xi} R_i F_{xi}^T)^{-1/2} F_{xi} \bar{c}_i \quad (3.13)$$

one obtains from (3.12) the relation

$$\bar{a}_i = \bar{a}_i - (F_{xi} R_i F_{xi}^T)^{-1/2} F_{ti} \cdot (\bar{t} - t) \quad . \quad (3.14)$$

The second term on the right-hand side of Eq. (3.14) is a slowly varying function. It can be interpreted geometrically as a distance between the true model surface $F_1(x; \bar{t}) = 0$ and the least squares model surface $F_1^*(x; t) = 0$, projected onto the space of reduced residuals. Correspondingly, $\bar{a}_i$ are the projections of the true residuals $\bar{c}_i$ onto a space that is orthogonal to the least squares model surface $F_1^*(x; t) = 0$. Because the last term in Eq. (3.14) is a slowly varying function, any scatter of $\bar{a}_i$ is directly reflected by the scatter of the a_i . Particularly, if the true errors $\bar{c}_i$ are normally distributed, then so are the projections $\bar{a}_i$ and, except for a slowly varying bias term, the reduced residuals a_i .

We notice that Eqs. (3.4), (3.13) and (3.14) permit one to express the least squares residuals c_i explicitly in terms of the real errors $\bar{c}_i$. Since the c_i are known from the adjustment, it would be more useful to express the $\bar{c}_i$ in terms of the c_i . This amounts to a solution of Eq. (3.12) for the $\bar{c}_i$ instead of c_i . However, in order to solve Eq. (3.12) for the c_i , we made use of Eq. (3.3), which is satisfied by the residuals c_i but not by the real errors $\bar{c}_i$. Therefore, one can determine from the residuals c_i only the reduced errors $\bar{a}_i$ and not the complete $\bar{c}_i$. This is the main reason for the introduction of the concept of a reduced residual space. Only in the special case where the dimension of the observable X_i is equal to the dimension of the constraint function F_i , Eq. (3.12) can be solved for either c_i or $\bar{c}_i$. But this is, of course, the case where the reduced residual space has the same dimension as the space of the observables, and the only important difference between $\bar{a}_i$ and $\bar{c}_i$ is that the components of the former are dimensionless.

In the vapor pressure problem one obtains from Eq. (3.7) the following definition of the reduced residuals a_i

$$a_i = \left[\left(\frac{c_{pi}/p_R}{1 + \theta_1 (p_i + c_{pi})/p_R} \right)^2 + \left(\frac{c_{Ti}}{\theta_2} \right)^2 \right]^{1/2} \text{sgn}(F_{pi}c_{pi} + F_{Ti}c_{Ti}), \quad (3.15)$$

where F_{pi} and F_{Ti} are partial derivatives of the constraint function (2.8a) or (2.8b) with respect to p_i and T_i . If only pressure is adjusted, then the corresponding definition of the reduced residuals is obtained from Eq. (3.15) by setting $c_{Ti} = 0$. For the vapor pressure problem the reduced residuals are scalars. Therefore, their distribution can be represented by a simple plot of cumulative distribution (a probit diagram), which permits a visual comparison with a normal distribution. Other tests and analyses for scalar residual distributions are discussed, e.g., in Draper and Smith.⁷

⁷Norman R. Draper and Harry Smith, *Applied Regression Analysis*, 2nd Edition, John Wiley & Sons, New York, NY, 1980.

IV. NUMERICAL EXPERIMENTS WITH SIMULATED DATA

Simulated vapor pressure data were obtained by choosing a set A, B, C of Antoine parameters, calculating $\hat{p}_i(\hat{T}_i)$ with Eq. (1.1) for s equidistant $\hat{T}_i$ values, and subtracting from the $\hat{p}_i$ and $\hat{T}_i$ random errors $\hat{c}_{pi}$ and $\hat{c}_{Ti}$ with known normal distributions. The simulated observations thus had the values

$$\begin{aligned} p_i &= \hat{p}_i - \hat{c}_{pi} , \\ T_i &= \hat{T}_i - \hat{c}_{Ti} , \end{aligned} \quad i = 1, \dots, s \quad (4.1)$$

Figure 1 shows a typical simulated set of 40 data points with corresponding error bars and the fitting curve with confidence limits. The Antoine parameters and the standard deviations $\hat{e}_{pi}$ and $\hat{e}_{Ti}$ of the random errors $\hat{c}_{pi}$ and $\hat{c}_{Ti}$, respectively, that were used in this example are listed in Table 1. Table 1 also contains the parameters of a fitting curve that is shown in Figure 1. These retrieved parameters correspond to the optimal value of the error parameter θ_1 . The error parameter θ_2 was set equal to zero for this evaluation of the data. The corresponding standard deviations of pressure and temperature observations are also listed in Table 1. The least squares model fitting was done by using the utility program COLSAC.⁸ The confidence limits that are shown in Figure 1 were calculated by solving the Antoine equation (1.1) for p and applying the linearized law of variance propagation to the function, i.e., by

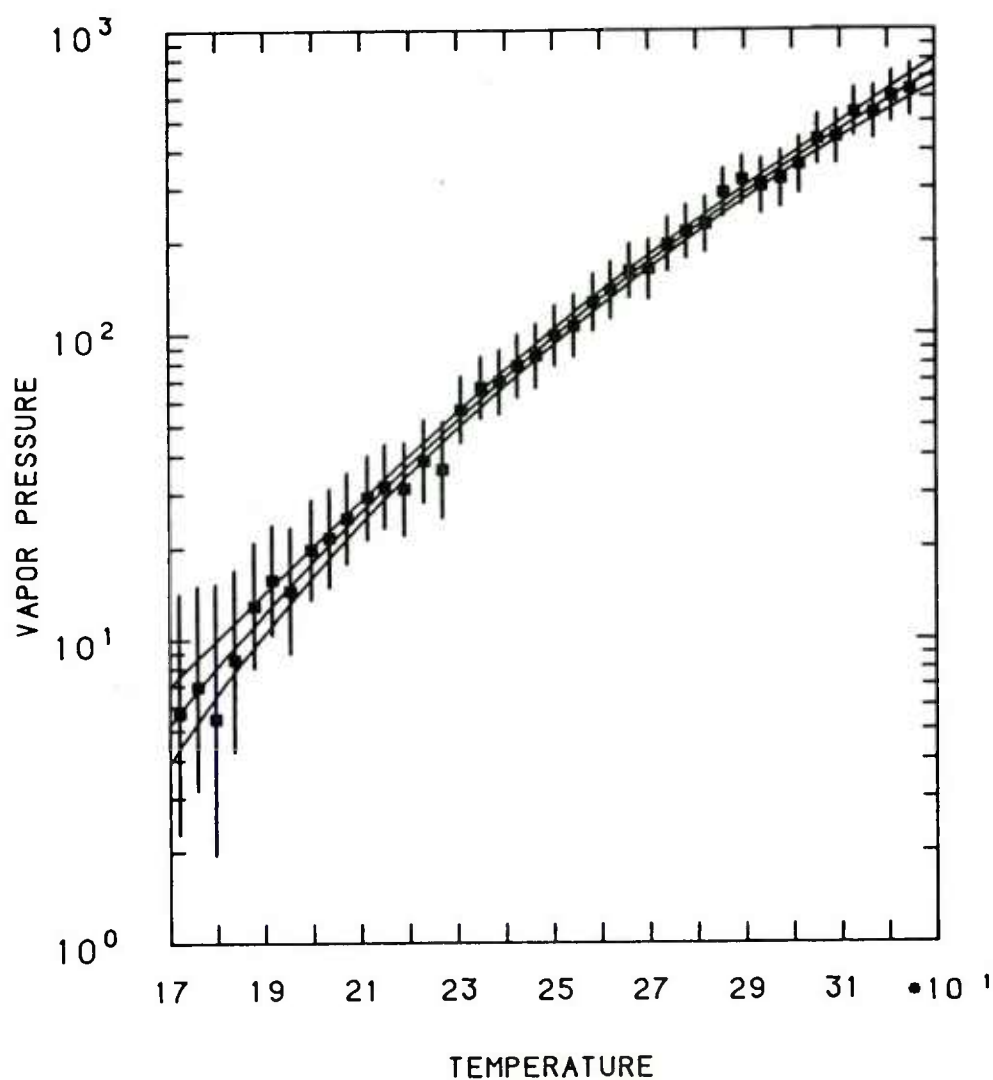
$$e_p = \left[\frac{\partial p(T; A, B, C)}{\partial (A, B, C)} V_{ABC} \left(\frac{\partial p(T; A, B, C)}{\partial (A, B, C)} \right)^T \right]^{1/2} , \quad (4.2)$$

where V_{ABC} is the variance-covariance matrix of the parameters A, B and C. The matrix V_{ABC} is defined as follows in terms of the standard errors of A, B and C and of the corresponding correlation matrix C_{ABC} (all given in Table 1):

$$V_{ABC} = D_{ABC} C_{ABC} D_{ABC} , \quad (4.3)$$

where D_{ABC} is a diagonal matrix with the standard errors in the diagonal. The distribution of the true reduced errors $\hat{a}_1$ (corresponding to the random errors $(\hat{c}_{pi}, \hat{c}_{Ti})$) is illustrated by Figure 2, that shows their cumulative distribution function compared with normal distribution.

⁸Aivars Celmiņš, "A Manual for General Least Squares Model Fitting," US Army Ballistic Research Laboratory Technical Report ARBRL-TR-02167, June 1979 (AD B040229L).



FITTED CURVE WITH 3.4 STANDARD ERROR CONFIDENCE LIMITS
OBSERVATIONS WITH 3.4 STANDARD ERROR ELLIPSES

Figure 1. Simulated Data with Fitted Curve

Error assumptions for the fitting:

$$e_{pi}/p_R = 1.20 + 0.056 (p_i + c_{pi})/p_R$$

$$e_{Ti} = 0.0 \text{ K}$$

Pressure is shown in torr and temperature is shown in °C.

TABLE 1. PARAMETERS OF SIMULATED DATA SHOWN IN FIGURE 1.

<u>Input Antoine Parameters</u>	<u>Retrieved Antoine Parameters</u>
A = 7.0	A = 7.567 ± 0.629
B = 1900 K	B = 2406 ± 551 K
C = 130 K	C = 181.39 ± 49.89 K
<u>Input Standard Errors</u>	<u>Retrieved Standard Errors</u>
$e_{pi}^*/p_R = 1.0 + 0.05 \frac{p_i^*}{p_R}$	$e_{pi}/p_R = 1.20 + 0.056 (p_i + c_{pi})/p_R$
$e_{Ti}^* = 0.1 \text{ K}$	$e_{Ti} = 0 \text{ (preset)}$
<u>Number of Data Sets</u>	<u>Correlation Coefficients</u>
s = 40	$c_{AB} = 0.998 \ 909 \ 7$
	$c_{AC} = 0.995 \ 506 \ 3$
	$c_{BC} = 0.998 \ 824 \ 7$

Figure 3 shows in the upper part a plot of the objective function S for this data set over the error parameter θ_1 , assuming $\theta_2 = 0$. For small θ_1 the error model (2.9) for e_{pi} approaches a constant pressure error assumption and S approaches the value 0.353. If θ_1 is large, the model approaches a constant relative error and a corresponding S value of 0.316. The transition between these limits is through a minimum of S at $\theta_1 = 0.046$ and $S = 0.233$. That minimum corresponds to the optimal θ_1 for this data set. The corresponding pressure standard error of the model is calculated by Eq. (2.9) and its numerical value is given in Table 1.

The lower part of Figure 1 shows a plot of the iterated parameter θ_1 that is computed by a minimization of S with fixed residuals, as in Step 3 of Nielsen's algorithm. The abscissa is again the parameter θ_1 and the ordinate is the ratio θ_1/θ_1 . Nielsen's algorithm converges to a point where the ratio equals one. The plot shows that $\theta_1/\theta_1 = 1$, indeed, is obtained in the vicinity of the minimum of S .

The distributions of the reduced residuals for small θ_1 , optimal θ_1 , and large θ_1 are shown in Figures 4, 5 and 6, respectively. We notice the interesting result that the distribution of reduced least squares residuals

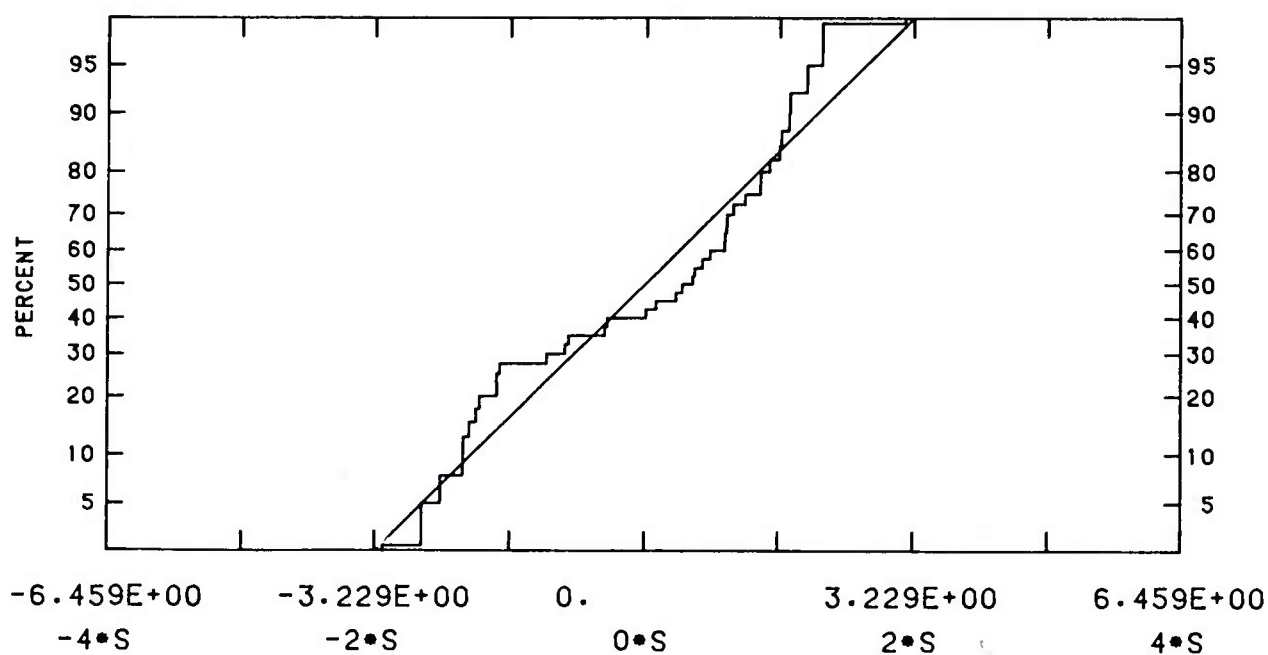
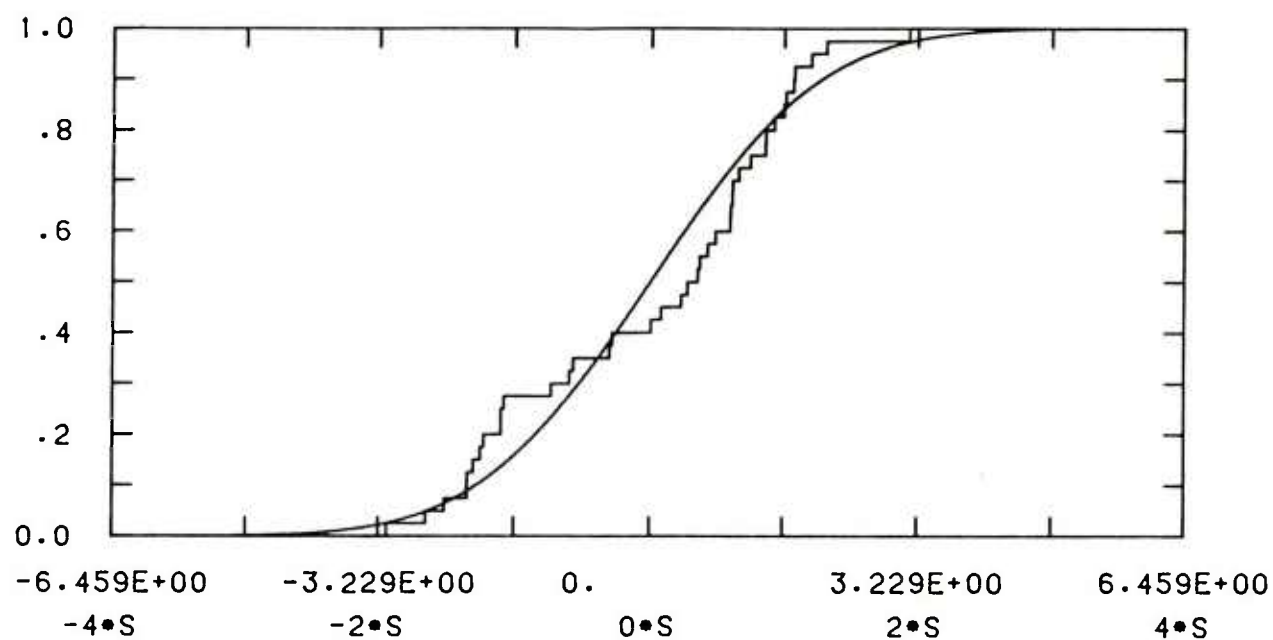


Figure 2. Distribution of Reduced True Errors of Simulated Data

Standard errors of the data are

$$e_{pi}/p_R = 1.0 + 0.05 \frac{p_i^*}{p_R}$$

$$e_{Ti} = 0.1 K$$

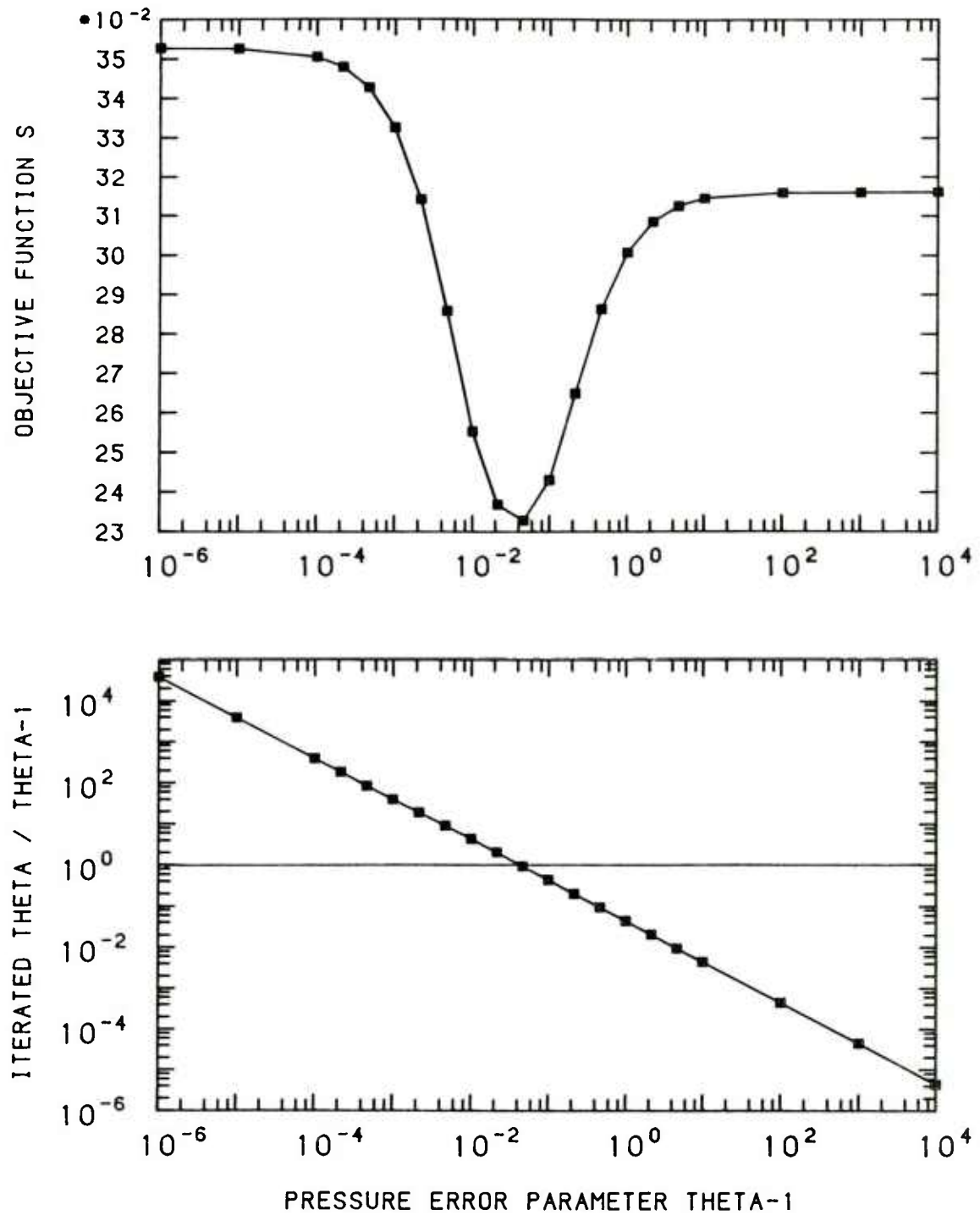


Figure 3. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for Simulated Data

Error parameter $\theta_2 = 0$

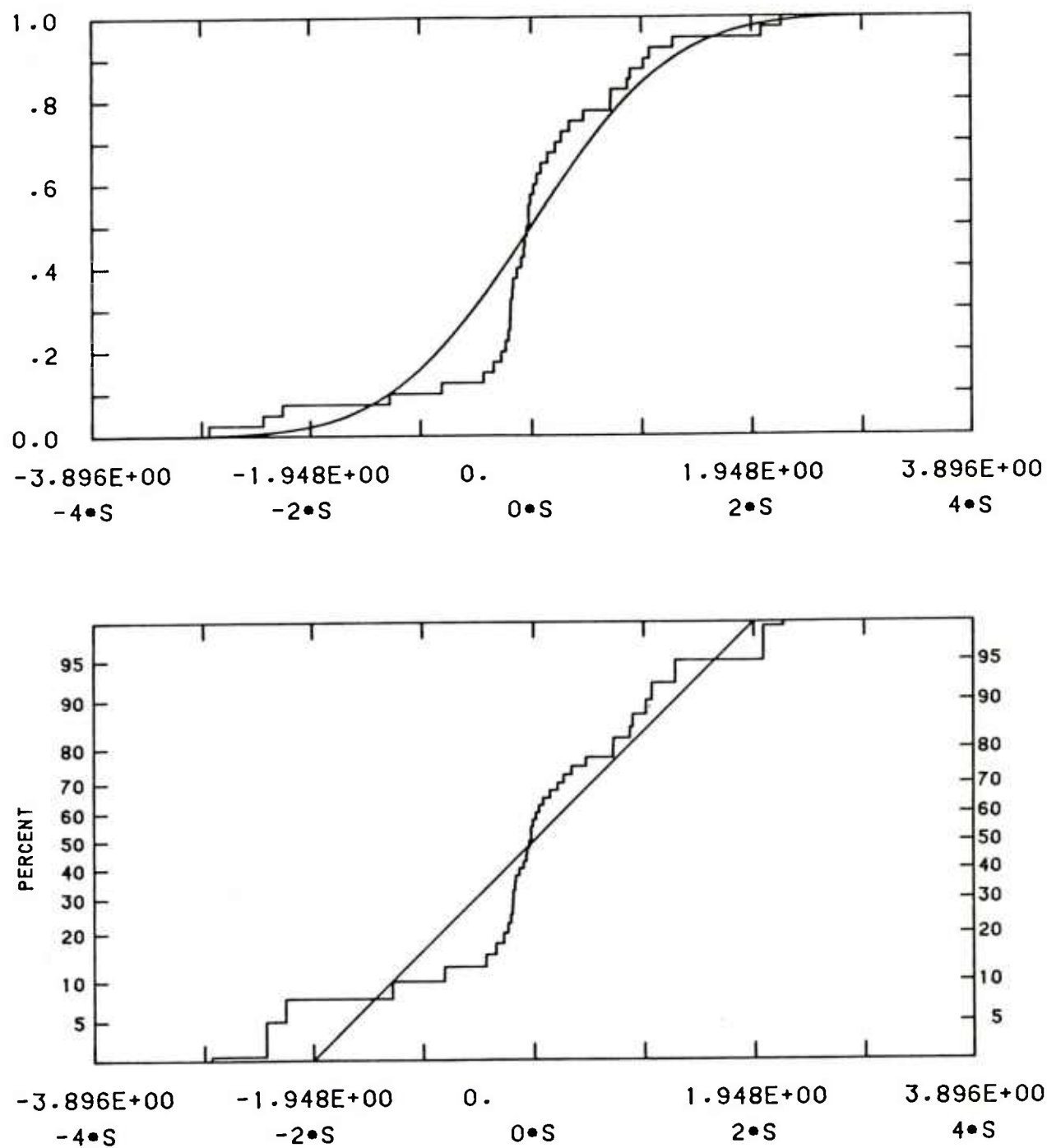


Figure 4. Distribution of Reduced Residuals for Simulated Data and Small Error Parameter θ_1

Error Parameter $\theta_2 = 0$

$S = 0.353$

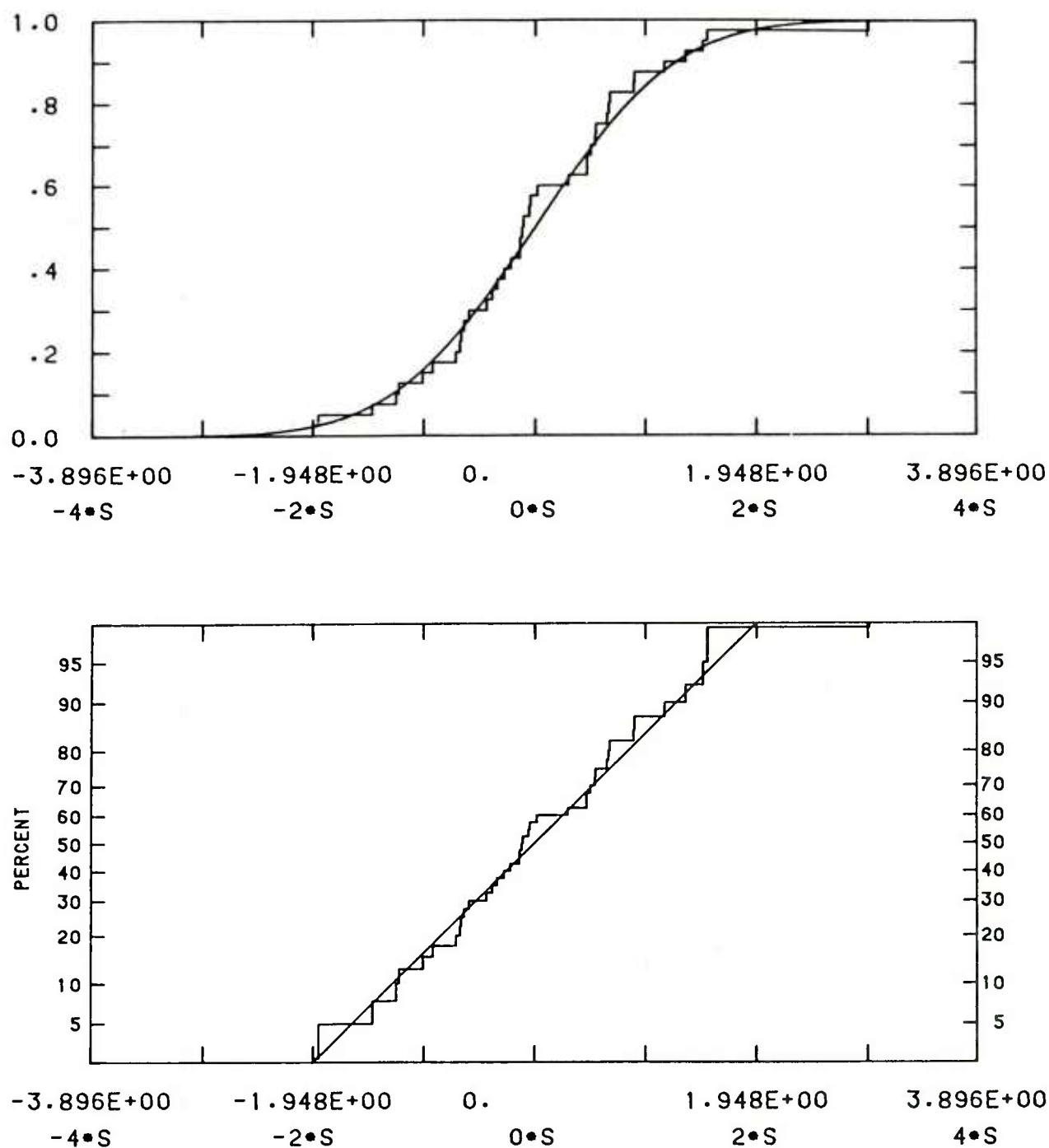


Figure 5. Distribution of Reduced Residuals for Simulated Data and Near Optimal Error Parameter $\theta_1 = 0.0464$

Error parameter $\theta_2 = 0$

$S = 0.233$

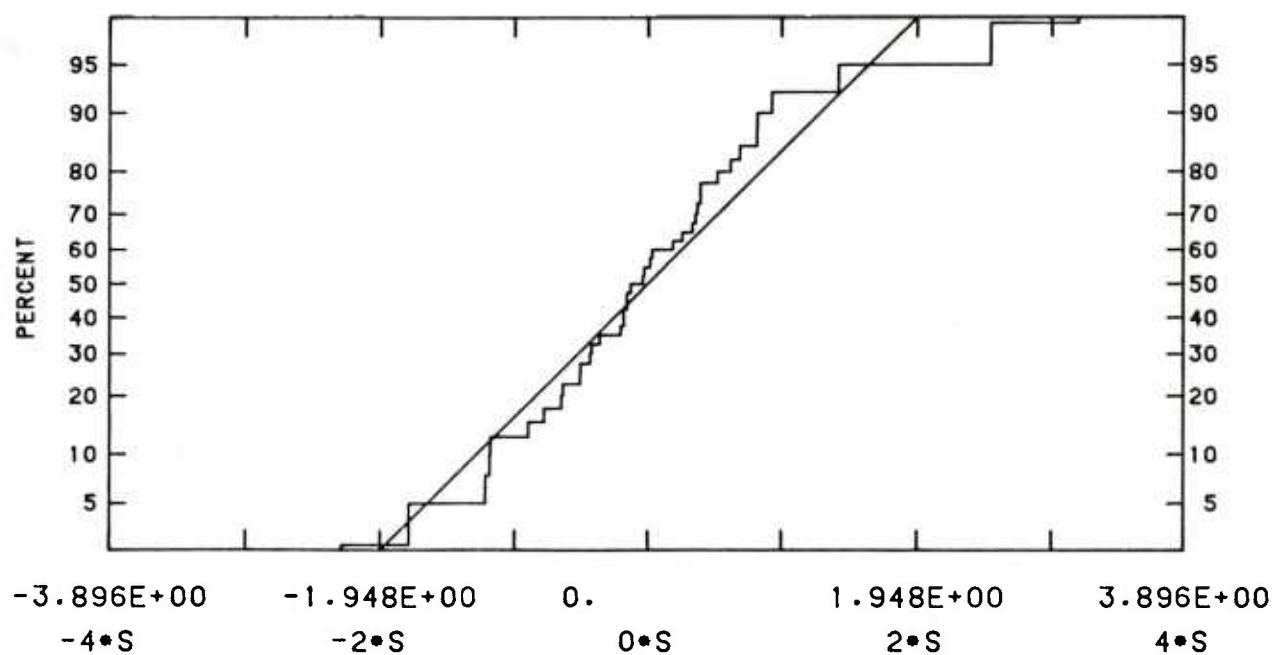
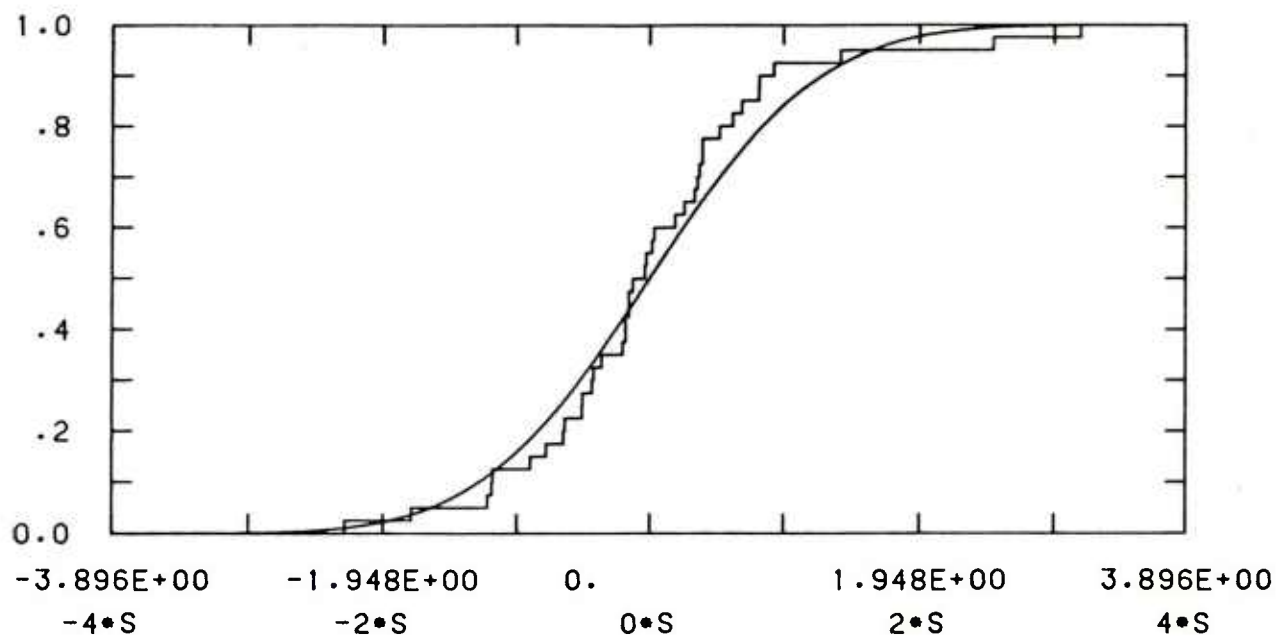


Figure 6. Distribution of Reduced Residuals for Simulated Data and Large Error Parameter θ_1

Error parameter $\theta_2 = 0$

$S = 0.316$

that corresponds to the optimal θ_1 (Figure 5) is much closer to a normal distribution than the distribution of the true reduced errors, shown in Figure 2.

Results from numerical experiments with sets of simulated data can be summarized as follows. The Nielsen algorithm produces reasonable approximations (within 20 percent) of the pressure error factors e_0 and e_{θ_1} if the temperature error is fixed and the number of data points is 50 or more. The algorithm converges in a few steps in these cases if a convergence acceleration formula is used. If both error parameters, θ_1 and θ_2 , are iterated, then one often needs an excessive number of iterations (60 or more), even in cases with large numbers of data points. If the number of data points is less than 50, then one can experience large deviations of the retrieved optimal error parameters from the corresponding input values. The minimization of S over θ for fixed residuals c was done using a simplex program.⁹ In some cases, the program failed to find a minimum of S , particularly in the vicinity of $\theta = 0$. This is an indication that S has little sensitivity to variations of θ in that region.

V. EXAMPLES OF TREATMENTS OF REAL DATA

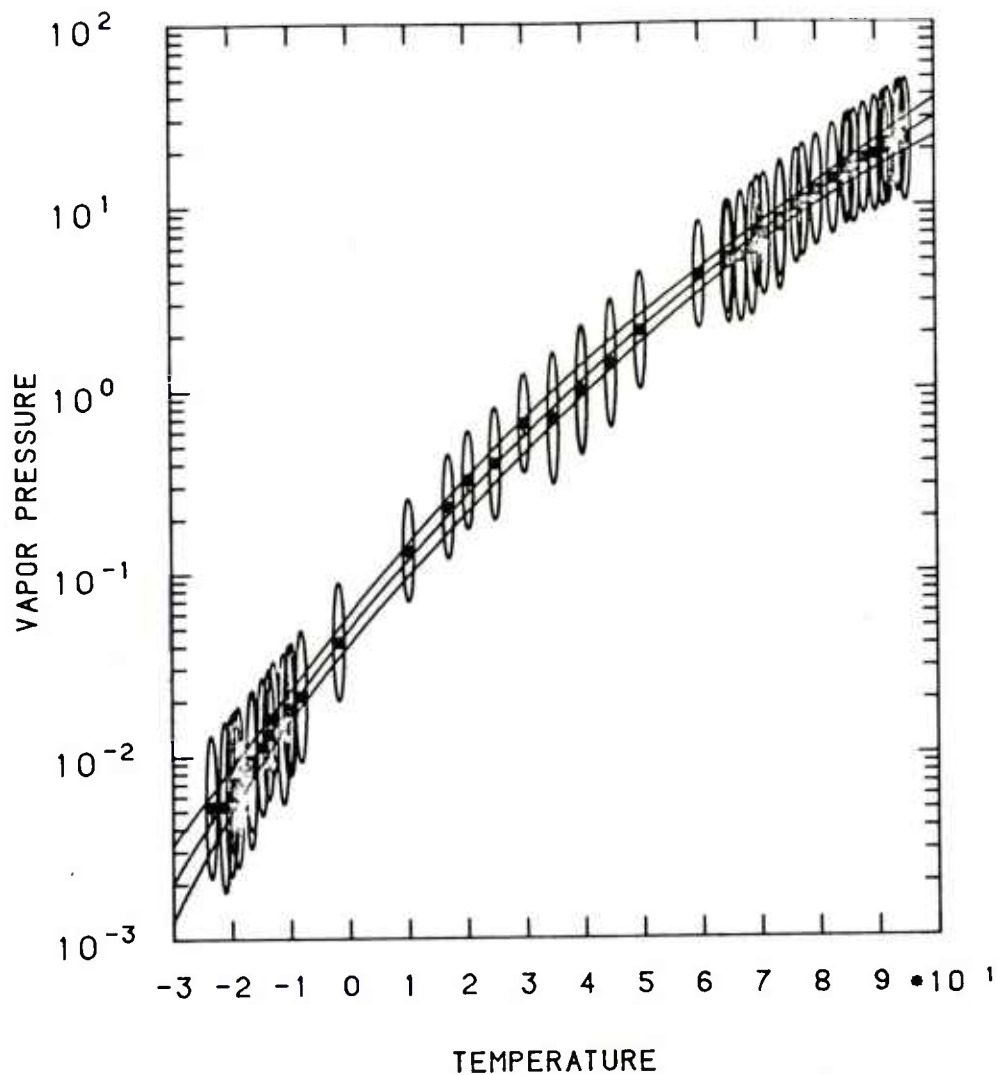
A set of vapor pressure data for the chemical compound GD has been published by Savage and Fielder.¹⁰ Figure 7 shows the data and the fitted curve for near optimal error parameter θ_1 and a temperature standard error of 0.1 K. The corresponding reduced residual distribution is shown in Figure 8, and the dependence of the objective function S on the parameter θ_1 is illustrated by Figure 9. The slight minimum of S is in this case located close to the place where $\theta_1/\theta_1 = 1$, so that Nielsen's iteration procedure, indeed, produces a near optimal value of θ_1 . However, if the standard error of the temperature measurements is assumed to be larger than in this example, then the $S(\theta_1)$ curve changes its shape and the transition between both limit values (for $\theta_1 = 0$ and $\theta_1 = \infty$) is not through a minimum. For example, if the temperature standard error is assumed to be 1.0 K, then the transition is through a maximum. (See Figure 10.) In such cases, the optimal value of θ_1 is either zero or infinity, whichever produces a smaller limit of S . For the compound GD data, the optimum is at infinity. Nielsen's algorithm is not applicable in such situations.

⁹Frederick S. Brundick, US Army ARRADCOM/Ballistic Research Laboratory, private communication, 1981.

¹⁰James J. Savage and Donald Fielder, "The Vapor Pressure of Chemical Agents GD, VX, EA 2223, EA 3347, EA 3580, EA 5365, and EA 5533," Edgewood Arsenal Technical Report EC-TR-76058, August 1976 (AD B013164L).

COMPOUND GD (SAVAGE AND FIELDER, 1976)

ITERATION STEP NR. 9



FITTED CURVE WITH 9.3 STANDARD ERROR CONFIDENCE LIMITS

OBSERVATIONS WITH 9.3 STANDARD ERROR ELLIPSES

Figure 7. Data and Fitted Curve for Compound GD

Error assumptions for the fitting:

$$e_{pi}/p_R = 1.68 \cdot 10^{-4} + 0.081 (p_i + c_{pi})/p_R$$

$$e_{Ti} = 0.10 \text{ K}$$

Pressure is shown in torr and temperature is shown in °C.

COMPOUND GD (SAVAGE AND FIELDER, 1976)

ITERATION STEP NR. 9

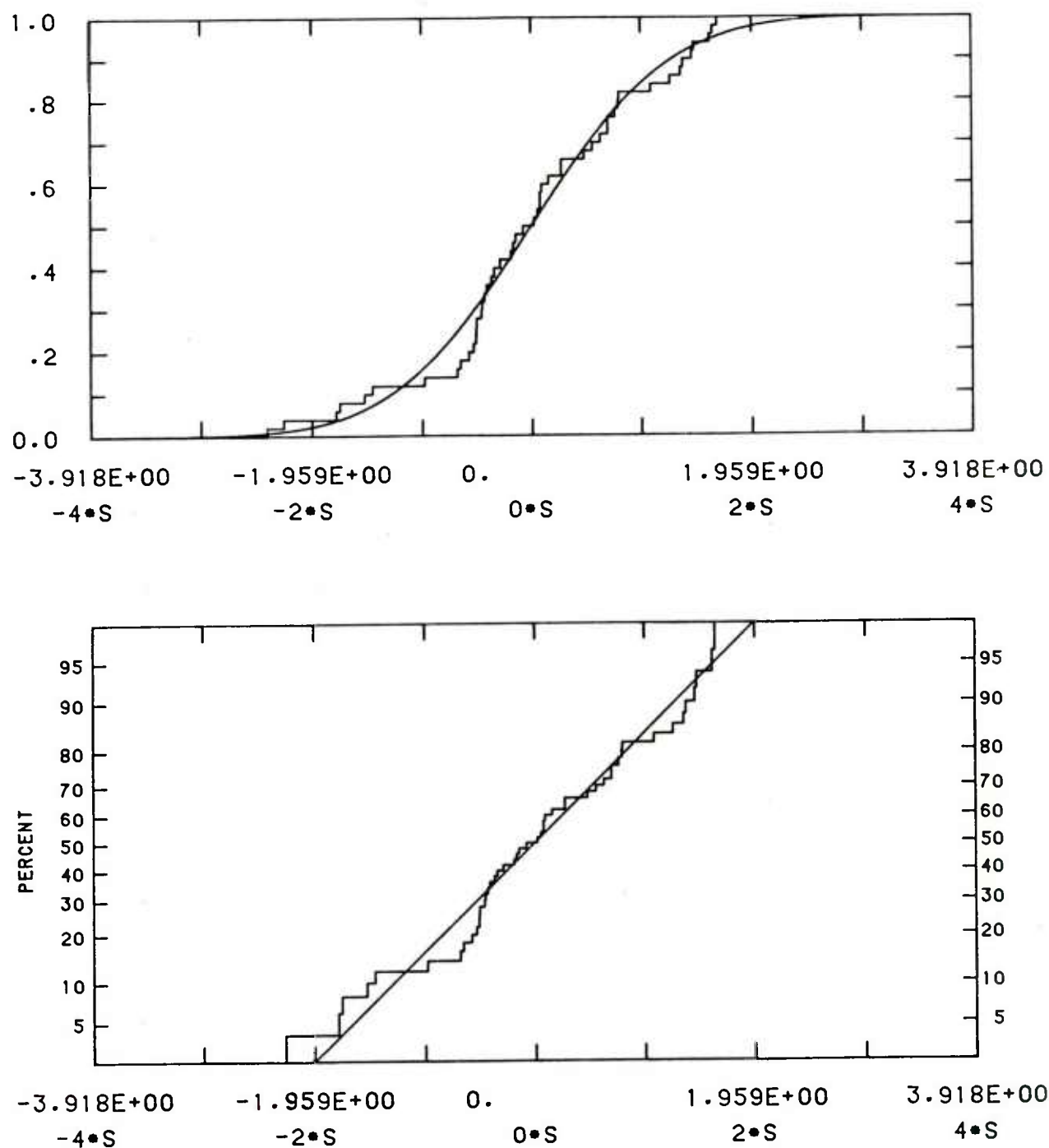


Figure 8. Distribution of Reduced Residuals for Compound GD and Near Optimal Error Parameters

Error assumptions are the same as for Figure 7.

COMPOUND GD (SAVAGE AND FIELDER, 1976)

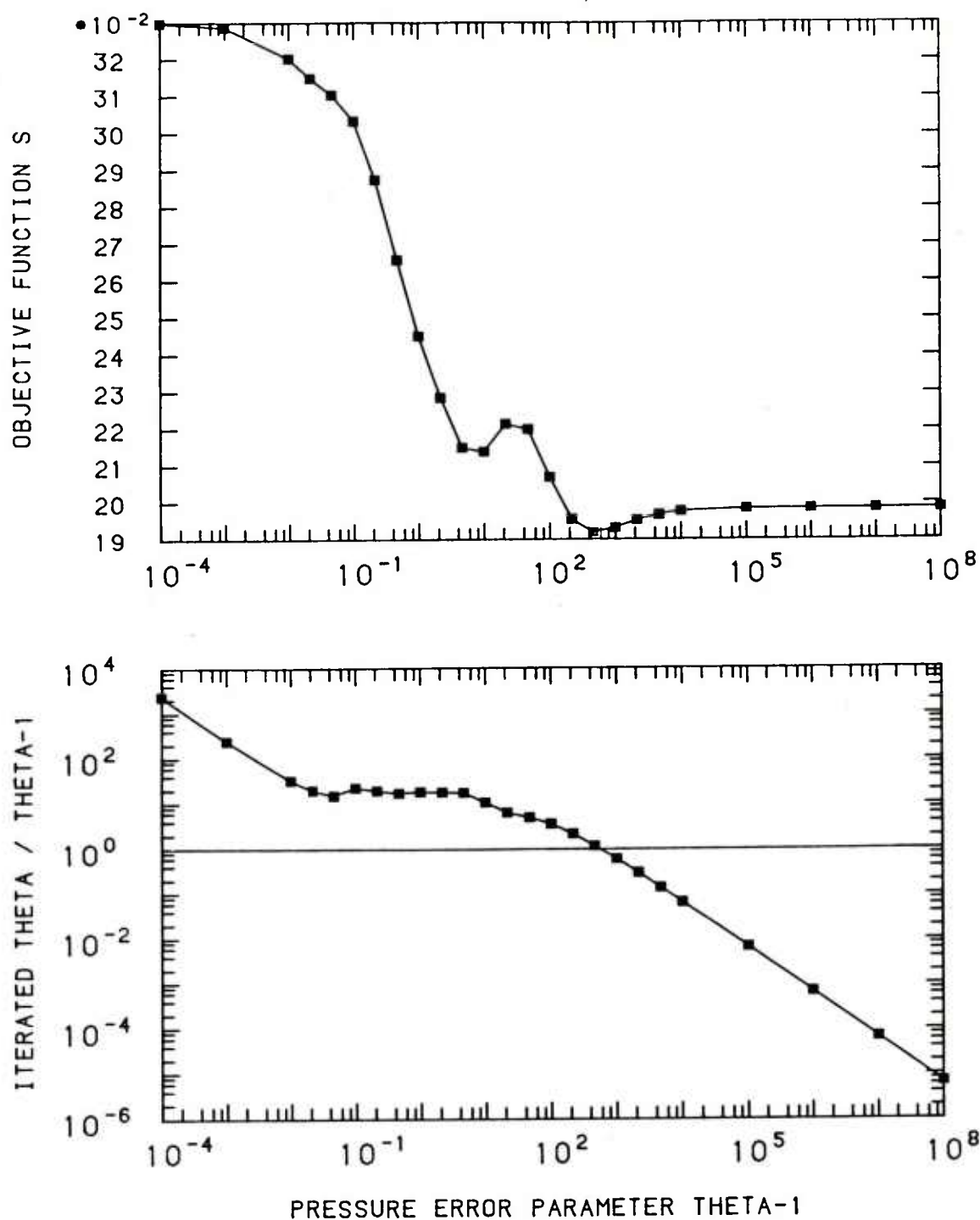


Figure 9. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for Compound GD

The error parameter θ_2 was chosen such that

$$e_{Ti} = e_o \theta_2 = 0.10 \text{ K}$$

COMPOUND GD (SAVAGE AND FIELDER, 1976)

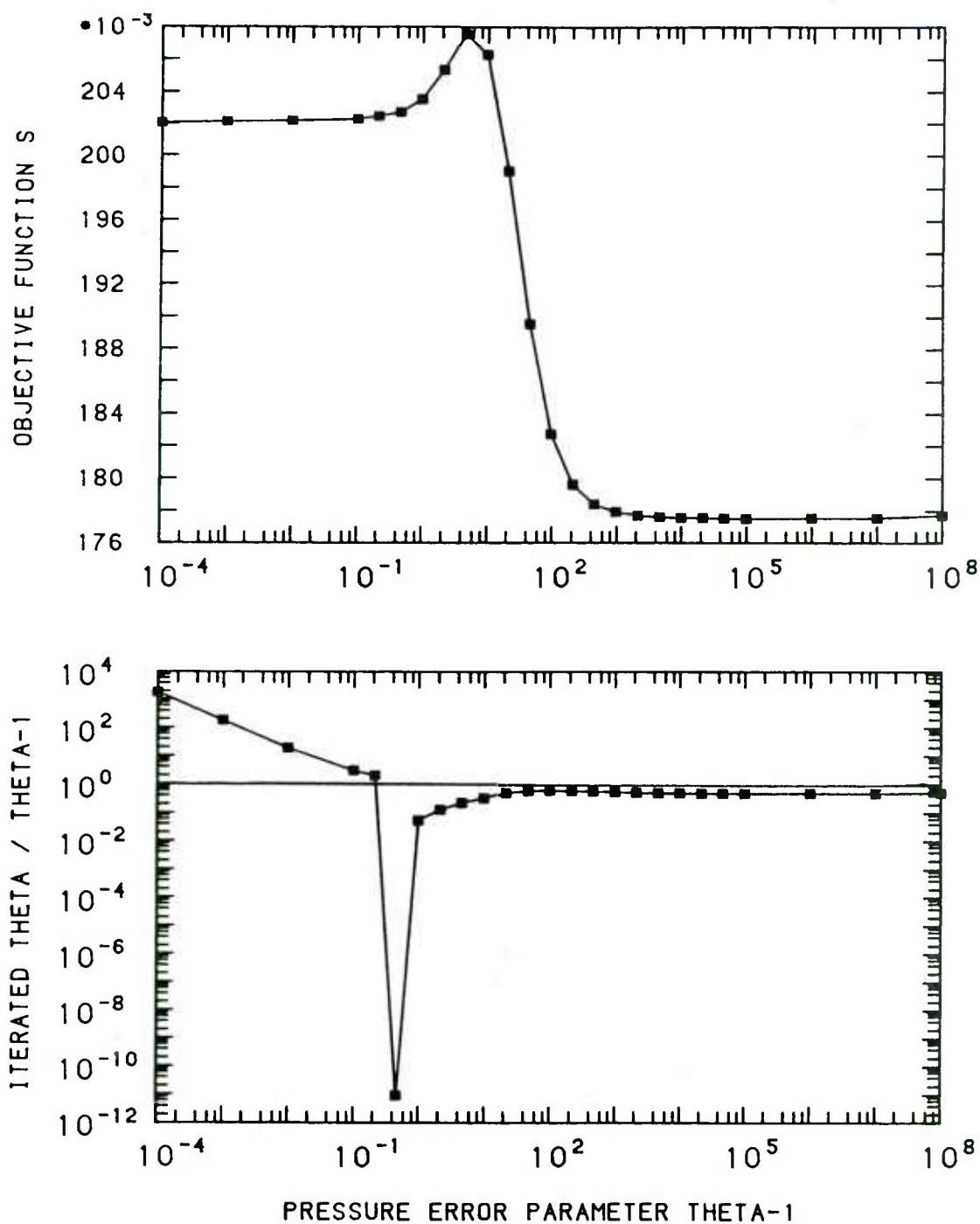


Figure 10. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for Compound GD

The error parameter θ_2 was chosen such that

$$e_{Ti} = e_o \theta_2 = 1.0 \text{ K}$$

The numerical results for the compound GD are summarized in Table 2, which also contains results reported by Savage and Fielder. The table shows that one obtains formally the best results (smallest standard errors and S) if a large temperature standard error is assumed. However, the difference between results with $e_T = 1.0$ K and $e_T = 0.0$ K are practically insignificant. Therefore, one can simply choose a fixed reasonable value of e_T consistent with the accuracy of the experimental procedure without sacrificing the quality of the other results. The Antoine constants by Savage and Fielder differ by about one standard error from the present result for $e_T = 0$. The difference is probably due to the particular constraint and least squares objective function formulation used by Savage and Fielder. That formulation is equivalent to a nonlinear variable transformation and, consequently, their results are not exactly minimizing the sum of pressure residual squares. (Effects of nonlinear variable transformations are discussed in Reference 11.)

A second example of vapor pressure data from Savage and Fielder¹⁰ is shown in Figure 11. The corresponding $S(\theta_1)$ -curve for $e_T = 0.1$ is shown in Figure 12. The transition between the limit values of S is in this case through a maximum. Consequently, the optimal θ_1 value is infinity. The iterated value θ_1 is for large θ_1 equal to a preset maximum which was included in the optimization program to avoid overflow. For smaller θ_1 values one obtains other iterates. In this example, the iterated $\theta_1(\theta_1)$ was found to be quite sensitive to the assumption about the temperature standard error. This is illustrated by Figure 13, which shows $S(\theta_1)$ and $\theta_1(\theta_1)$ for $e_T = 0$. The S function is practically the same as in Figure 11, but the iterated $\theta_1(\theta_1)$ obviously has changed its behavior in the range of θ_1 between 10^{-2} and 10^3 .

Numerical results for the compound VX data are given in Table 3. The difference between the present results and those of Savage and Fielder again is about one standard error. This agreement is remarkable, because Savage and Fielder used additional data for their analysis covering an almost three times larger temperature range than available for the present analysis. The predicted boiling temperature is in the present analysis about 24 K lower than predicted by Savage and Fielder. This difference is less than the estimated standard error of our prediction; that is, the difference is compatible with the accuracy of the observations. The relatively large size of the estimated standard error is a consequence of the large extrapolation from 100°C to 274°C (5 torr to 760 torr). Savage and Fielder had more data available over a larger temperature range and extrapolated only from 231°C to 298°C (140 torr to 760 torr). Their predicted boiling temperature is, therefore, probably more accurate than ours. However, they do not provide error estimates of their results.

¹¹Aivars Celminš, "Least Squares Model Fitting with Transformations of Variables," *Journal for Statistical Computation and Simulation*, Vol. 14, pp 17-39, 1981.

TABLE 2. ADJUSTMENT RESULTS FOR COMPOUND GD

	Present Analysis			Savage and Fielder ¹⁰
	$e_T = 1.0 \text{ K}$	$e_T = 0.1 \text{ K}$	$e_T = 0$	$e_T = 0$
Optimal e_p/p_R	$0.0364p/p_R$	$1.42 \cdot 10^{-4} + 0.0789p/p_R$	$1.38 \cdot 10^{-4} + 0.0794p/p_R$	$\sim p/p_R$
A	8.089 ± 0.319	7.837 ± 0.333	7.855 ± 0.333	7.4709
B (K)	2222 ± 173	2100 ± 174	2099 ± 174	1903.1
C (K)	236.2 ± 10.3	229.0 ± 10.6	229.0 ± 10.6	216.87
c_{AB}	0.998 7996	0.998 8284	0.998 8313	----
c_{AC}	0.994 8105	0.995 3708	0.995 3934	----
c_{BC}	0.998 5390	0.998 7951	0.998 8036	----
S	0.1775	0.1920	0.1923	----
Boiling Temp. in $^{\circ}\text{C}$	190.41 ± 3.28	192.94 ± 3.90	192.93 ± 3.92	198

The c_{AB} , c_{AC} and c_{BC} are correlation coefficients between the Antoine constants A, B, and C. The boiling temperature is quoted for 101.3 kPa (760 torr) pressure. The temperature range of observations is between 243.15 and 463.15 K (-30 and 190°C).

COMPOUND VX (SAVAGE AND FIELDER, 1976)

ITERATION STEP NR. 1

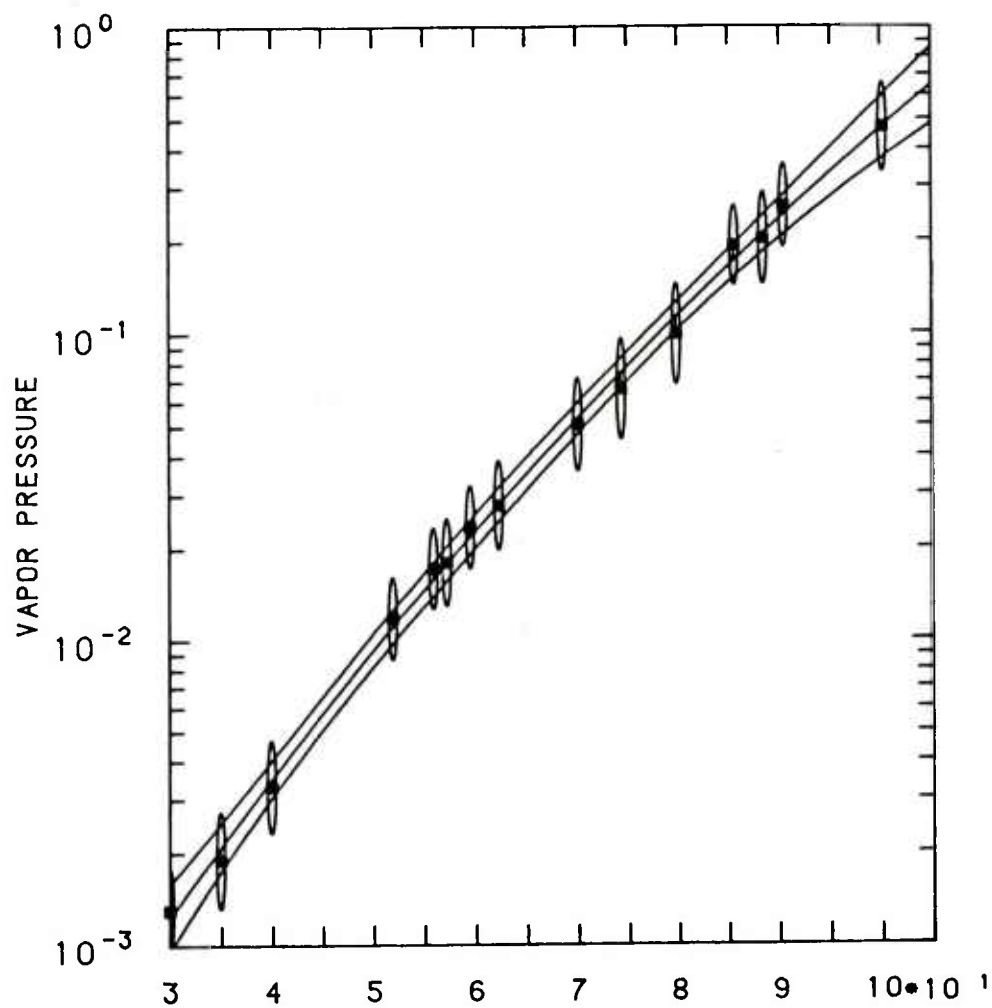


Figure 11. Data and Fitted Curve for Compound VX

Error assumptions for the fitting:

$$e_{p_i}/p_R = 0.0025 (p_i + c_{p_i})/p_R$$

$$e_{T_i} = 0.10 \text{ K}$$

Pressure is shown in torr and temperature is shown in °C.

COMPOUND VX (SAVAGE AND FIELDER, 1976)

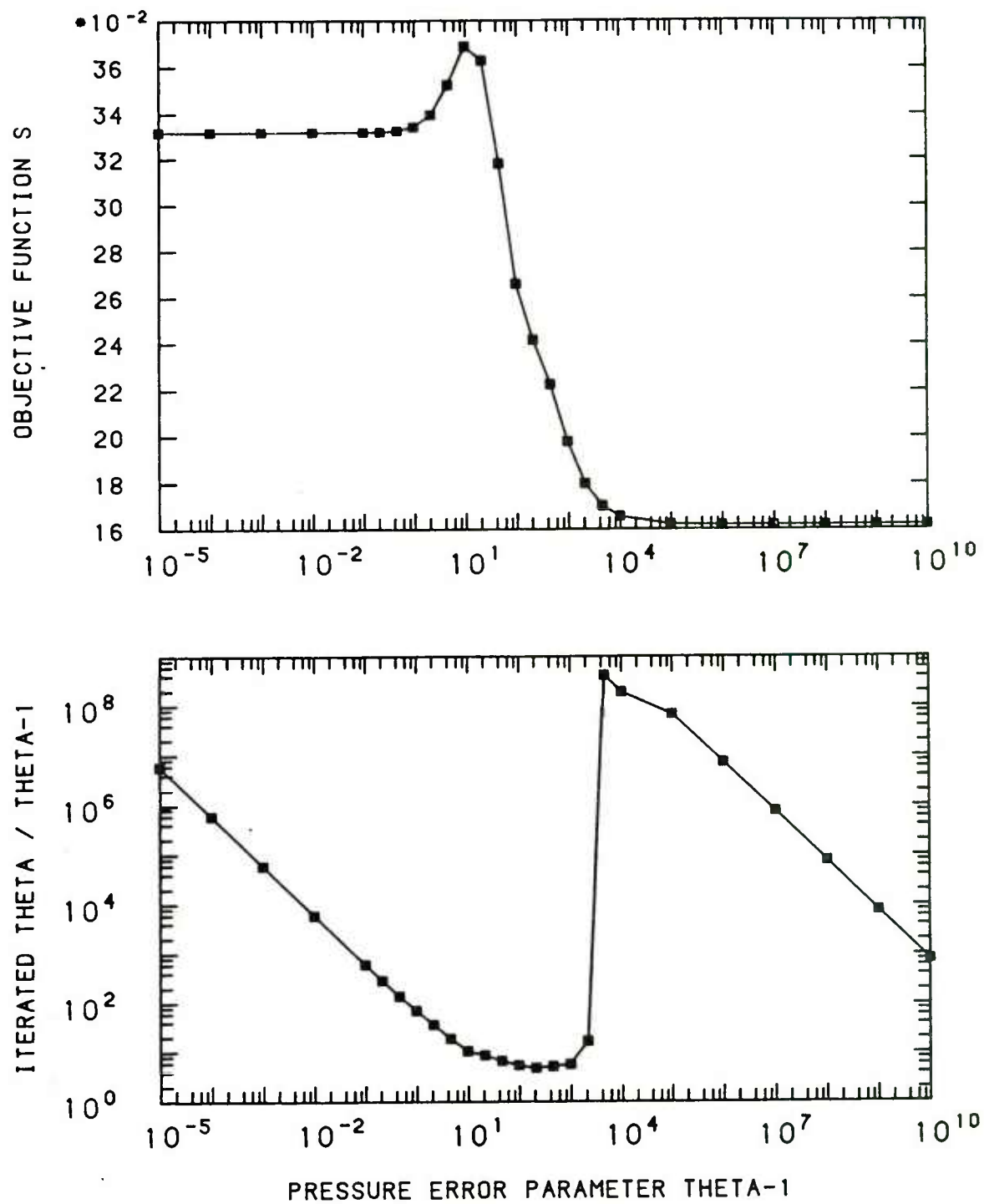


Figure 12. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for Compound VX

The error parameter θ_2 is chosen such that

$$e_{Ti} = e_o \theta_2 = 0.10 \text{ K}$$

COMPOUND VX (SAVAGE AND FIELDER, 1976)

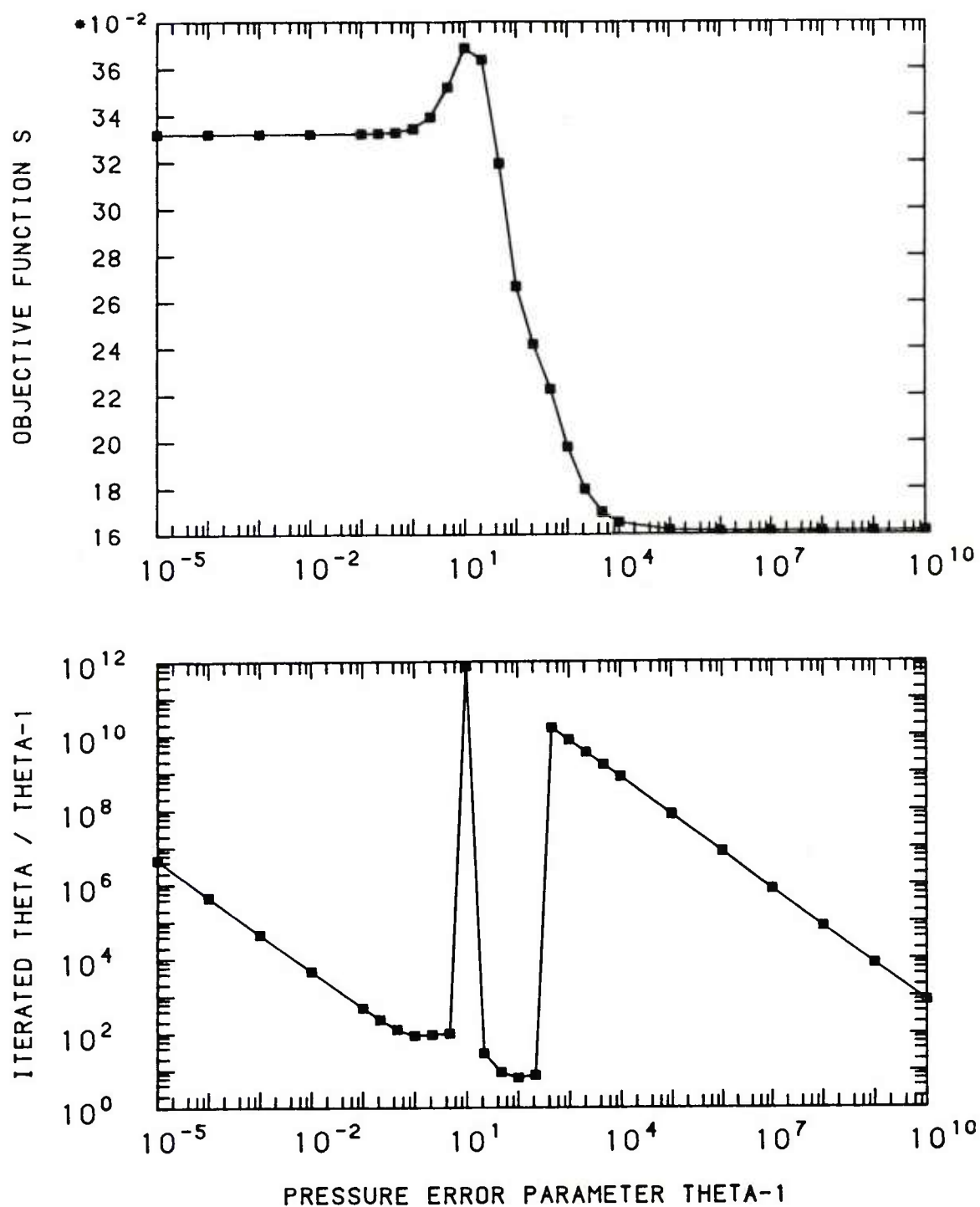


Figure 13. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for Compound VX

The temperature standard error is assumed to be zero.

TABLE 3. ADJUSTMENT RESULTS FOR COMPOUND VX

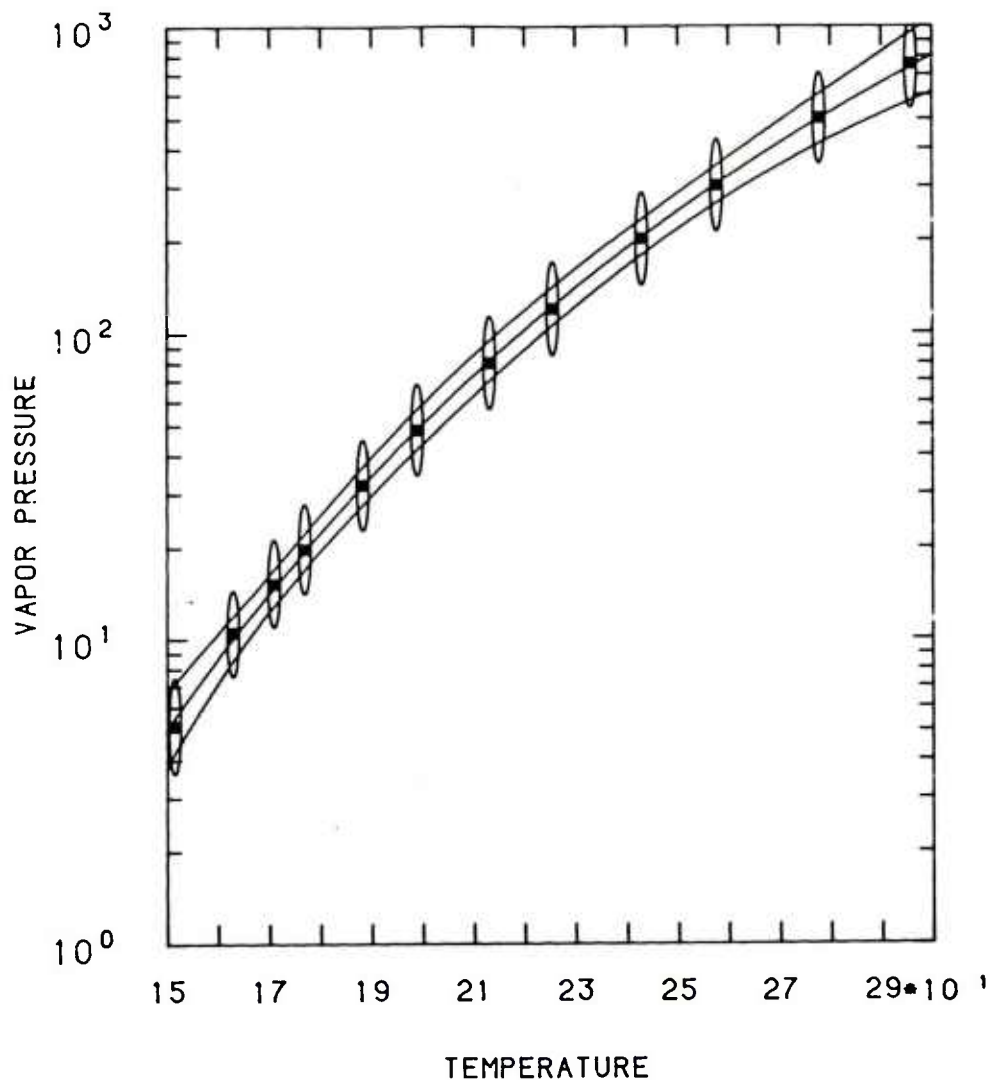
	Present Analysis		Savage and Fielder ¹⁰
	$e_T = 0.1 \text{ K}$	$e_T = 0$	$e_T = 0$
Optimal e_T/p_R	0.0825 p/p_R	0.0829 p/p_R	$\sim p/p_R$
A	8.710 ± 1.793	8.708 ± 1.793	7.2810
B (K)	2852 ± 994	2851 ± 993	2072.1
C (K)	215.4 ± 48.1	215.4 ± 48.0	172.54
c_{AB}	0.999 380 8	0.999 381 6	----
c_{AC}	0.997 526 4	0.997 530 5	----
c_{BC}	0.999 375 2	0.999 376 4	----
S	0.1616	0.1620	----
Boiling Temp. (°C)	273.9 ± 28.2	273.9 ± 28.2	298

The c_{AB} , c_{AC} are correlation coefficients between the Antoine constants A, B and C. The boiling temperature is quoted for 101.3 kPa (760 torr) pressure. The temperature range of observations was between 303.15 and 373.35 K (30 and 100.2°C) for the present analysis and between 303.15 and 504.15 K (30 and 231°C) for the Savage and Fielder¹⁰ analysis.

As a last example, we show the results of the analysis of vapor pressure data for 1-Tetradecanol. The data are taken from Kemme and Kreps¹ and shown in Figure 14. The corresponding objective function $S(\theta_1)$ and iterate $\theta_1(\theta_1)$ are shown in Figure 15. The erratic behavior of $\theta_1(\theta_1)$ in Figure 15 is possibly due to a failure of the simplex algorithm to locate the proper minimum, indicating that the problem is rather delicate numerically. The detailed behavior of $S(\theta_1)$ and $\theta_1(\theta_1)$ is very sensitive to assumptions about the accuracy of temperature measurements, as illustrated by the different curves in Figure 15 and 16, respectively. However, in both analyzed cases, i.e., for temperature standard error 0.1 K and zero, the optimal value of the error parameter θ_1 is infinity. The numerical results for the 1-Tetradecanol data are summarized in Table 4. The present results closely agree with those of Penski and Latour. The differences are likely

1-TETRADECANOL (KEMME AND KREPS, 1969)

ITERATION STEP NR. 1



FITTED CURVE WITH 11.9 STANDARD ERROR CONFIDENCE LIMITS

OBSERVATIONS WITH 11.9 STANDARD ERROR ELLIPSES

Figure 14. Data and Fitted Curve for 1-Tetradecanol

Error assumptions for the fitting are

$$e_{pi}/p_R = 0.0294 (p_i + c_{pi})/p_R$$

$$e_{Ti} = 0.1 \text{ K}$$

Pressure is shown in torr and temperature is shown in $^{\circ}\text{C}$.

1-TETRADECANOL (KEMME AND KREPS, 1969)

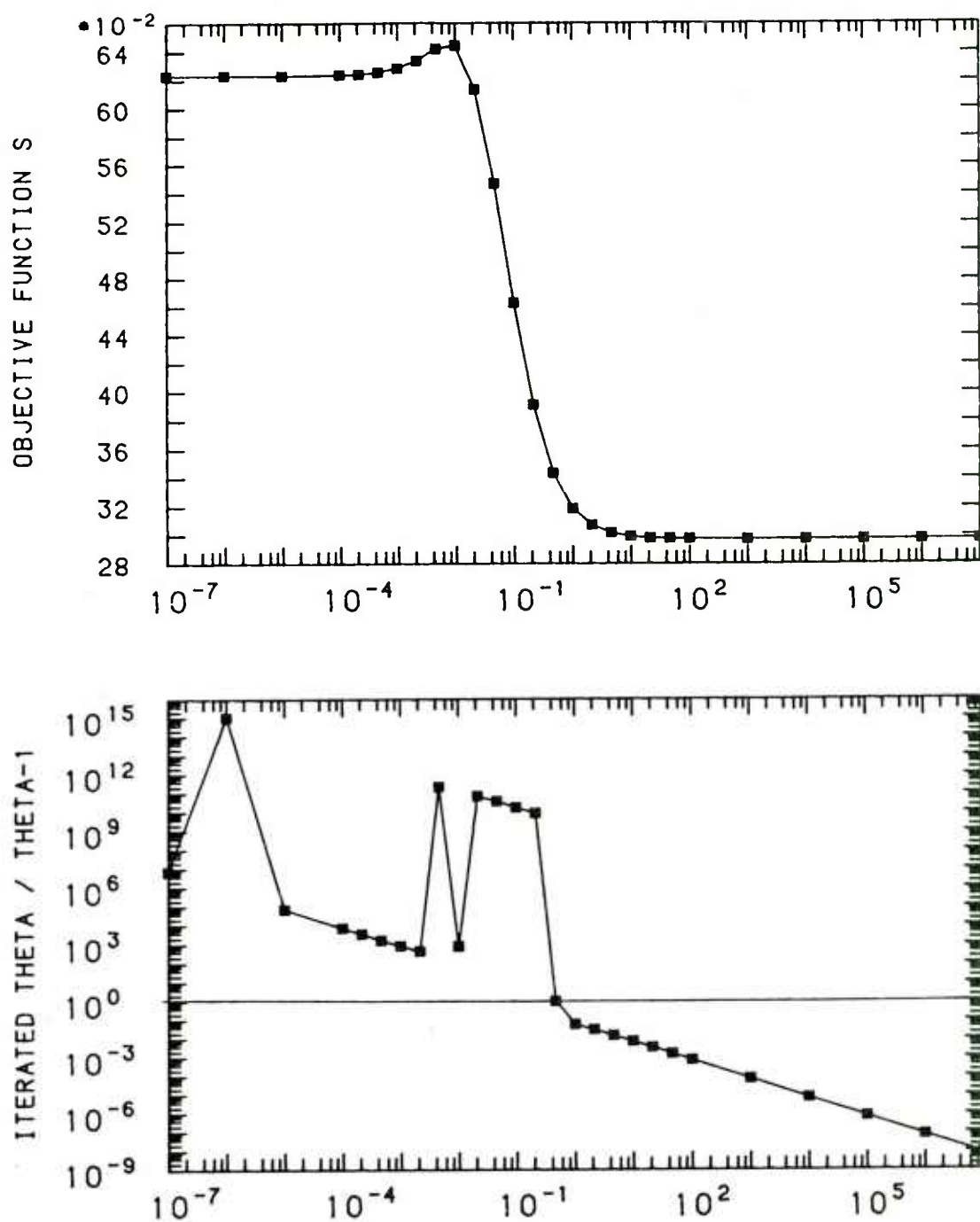


Figure 15. Objective Function S and Iterated Error Parameter Ratio θ_1 / θ_1 for 1-Tetradecanol

The error parameter θ_2 is chosen such that

$$e_{Ti} = e_{\theta_2} = 0.10 \text{ K}$$

1-TETRADECANOL (KEMME AND KREPS, 1969)

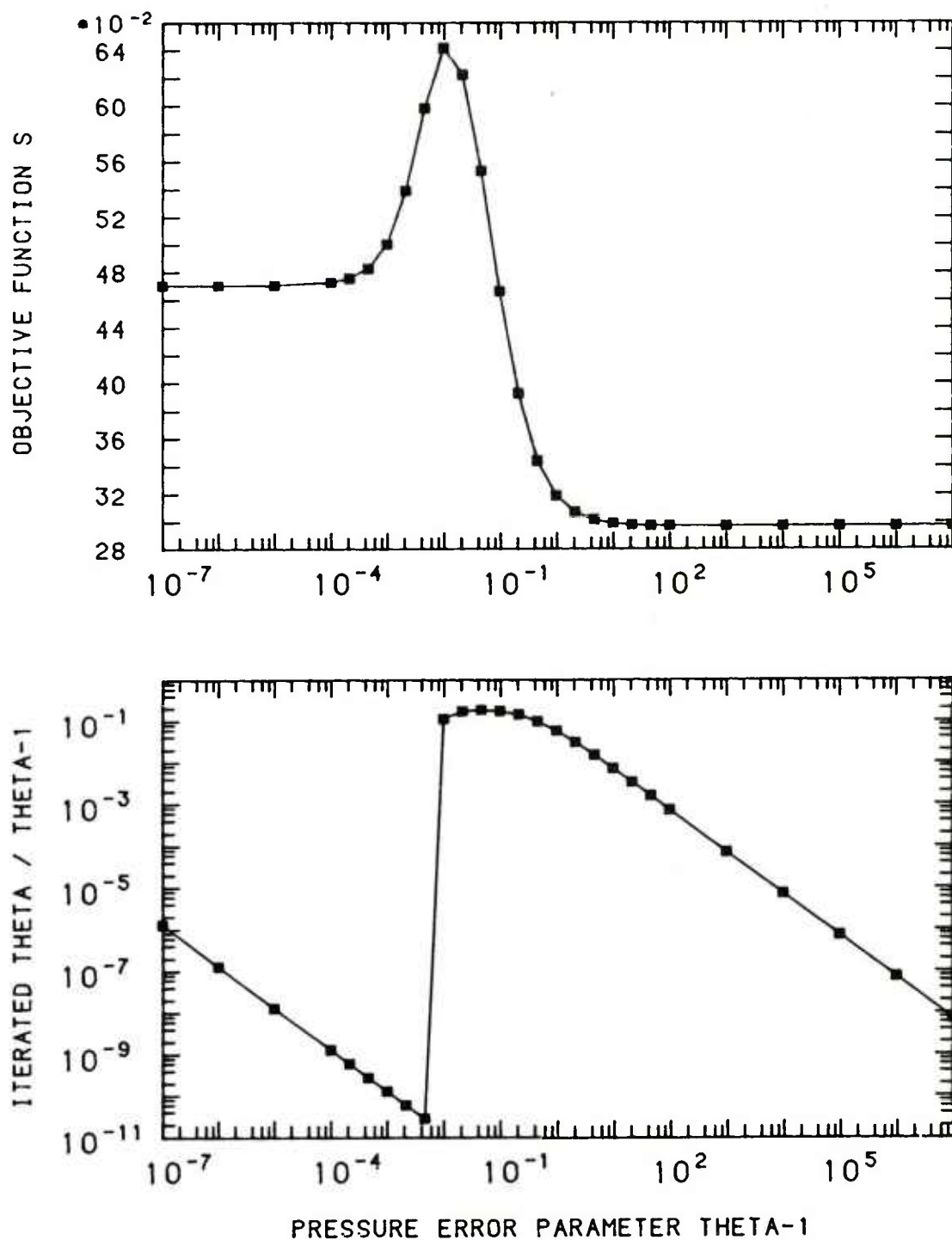


Figure 16. Objective Function S and Iterated Error Parameter Ratio θ_1/θ_1 for 1-Tetradecanol

The temperature standard error is assumed to be zero.

TABLE 4. ADJUSTMENT RESULTS FOR 1 - TETRADECANOL

	Present Analysis		Kemme and Kreps ¹	Penski and Latour ²
	$e_T = 0.1 \text{ K}$	$e_T = 0$	$e_T = 0$	$e_T = 0$
Optimal e_p/p_R	0.0294 p/p_R	0.0294 p/p_R	$\sim p/p_R$	$\sim p/p_R$
A	6.2284 $\pm$ 0.1846	6.2251 $\pm$ 0.1851	6.4840	6.21962
B (K)	1250.2 $\pm$ 106.3	1248.2 $\pm$ 106.7	1412.907	1244.90
C (K)	76.23 $\pm$ 12.02	76.01 $\pm$ 12.06	95.368	75.600
c_{AB}	0.997 527 0	0.997 525 0	-----	-----
c_{AC}	0.991 019 0	0.991 025 3	-----	-----
c_{BC}	0.997 877 0	0.997 882 1	-----	-----
S	0.2974	0.2973	-----	-----
Boiling Temp. ($^{\circ}\text{C}$)	297.23 $\pm$ 1.07	297.24 $\pm$ 1.08	-----	297.258

The c_{AB} , c_{AC} and c_{BC} are correlation coefficients between the Antoine parameters A, B, and C. The boiling temperature is quoted for 101.3 kPa (760 torr) pressure. The temperature range of observations is between 425.15 and 569.15 K (152 and 296 $^{\circ}\text{C}$).

due to the effect of nonlinear data transformation mentioned above. This effect is smaller than in the case of compound GD because the temperature range of the observations is smaller. The difference between the present results and those of Kemme and Kreps is between one and two standard errors of the Antoine parameters. It is not clear how Kemme and Kreps obtained the Antoine parameters, but their values are between the values corresponding to $e_p \sim p$ and constant e_p . We obtained almost the same Antoine parameters as Kemme and Kreps if we assumed for the pressure standard errors the formula

$$e_{pi}/p_R = 0.139 + 0.0139 (p_i + c_{pi})/p_R$$

and $e_{Ti} = 0$. The corresponding value of S is 0.4663, indicating that this choice of error models is not optimal.

VI. CONCLUSIONS

A posteriori estimation of measurement accuracy is usually based on a postulated mathematical model of the observed event and an analysis of the corresponding residuals. In addition, one generally assumes that the dimension of the model equation is equal to the dimension of the observables. With these assumptions one can handle, for instance, curve or surface fitting with only one variable subject to errors and repeated measurements with arbitrary dimensions. In general, however, the dimension of the model equation can be less than the dimension of the observations, for instance, if a curve or surface is fitted to observations with errors in more than one component. The usual techniques of residual analysis cannot be directly applied to such cases because the model equations effectively reduce the dimensionality of the residuals by generating correlations between the components of the residuals. In order to treat such cases, we introduced a new concept of reduced residuals. These residuals have the proper dimensionality and can be analyzed by available methods. Particularly, in the case of vapor pressure measurements (planar curve fitting with both components subject to error) the reduced residuals are one-dimensional and can be analyzed by well-known methods that have been developed for scalar residuals.

In the particular error estimation technique considered here, one determines the residuals by least squares model fitting and postulates as optimal a close to normal distribution of the reduced residuals. As a measure for the normality of the distribution one chooses a negative entropy function S , as suggested in the literature, whereby the distribution is considered optimal if S is a minimum. The technique consists of a

systematic variation of the measurement error estimates until a minimum of S is obtained. Our numerical experiments with vapor pressure data have shown that this procedure, indeed, produces reduced residuals that have a close to normal distribution. We were also able to retrieve by this procedure approximate standard errors from simulated measurements with known normal error distributions. Reasonable accuracy of the retrieved errors was obtained with 50 or more observation sets per fitted curve. However, an automatic determination of measurement standard errors (as suggested in the literature) is not generally possible. We suggest, instead, an interactive direct search for the minimum of S .

In summary, a combination of the new concept of reduced residuals and the use of an objective function S allows one to estimate a posteriori the standard errors of pressure as well as temperature measurements. The technique is applicable to general model fitting situations, including cases with arbitrary dimensions. The particular choice of the entropy function S as a measure for the goodness of the distribution of the reduced residuals is arbitrary and other objective functions also can be used in the described process. We have not tried to determine whether the entropy function is the best choice but it has produced reasonable results in our examples.

ACKNOWLEDGEMENT

The author wishes to thank Mr. Chris Roler for programming help.

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11. Aivars Celmiņš, "Least Squares Model Fitting with Transformations of Variables," Journal for Statistical Computation and Simulation, Vol. 14, pp. 17-39, 1981.

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