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A New Method for Optimizing the Structure of Thermodynamic Correlation Equations

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Dedicated to Prof. Dr. phil. F. Kohler on the Occasion of His 65th Birthday

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An optimization strategy is presented for optimizing the structure of empirical thermodynamic correlation equations. Based on a comprehensive functional expression for the physical dependence considered, which is called a "bank of terms," the new procedure optimizes the structure and the length of the equation as well. The application of this method results in an equation which meets the quality wanted for representing the experimental data with the lowest number of fitted coefficients. The procedure can be used for the determination of the structure of any equation where the method of the linear least squares is applicable. A detailed description of the algorithm is given which includes values for the control parameters for different applications in the field of thermodynamics (vapor pressure equations, equations of state, etc.) and also for applications in other fields. The optimization steps are described using an equation which represents a relationship between variables in a general form. It is demonstrated how even the complex problem of the optimization of a fundamental equation for the Helmholtz energy can be written in terms of this general equation.

KEY WORDS: correlation equation; equation of state; least-squares principle; optimization method; search method.

1. INTRODUCTION

The design of processes and apparatus in the field of chemical engineering and energy technology requires effective equations for calculating the thermophysical properties of the working fluid considered. Of course, it would be best if we had simple equations which are theoretically founded and

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accurate enough over the entire fluid region. Since, however, statistical thermodynamics has not yet achieved such a standard, in most cases, one must use empirical equations which are based on correspondingly accurate experimental data covering the entire fluid region of interest.

Examples of such empirical correlation equations are

- expressions for thermal and caloric properties along the vapor–liquid coexistence curve (vapor pressure, densities and enthalpies of the saturated liquid and vapor);
- equations for the activity coefficients or the excess Gibbs energy of fluid mixtures;
- wide-range equations for the transport properties viscosity and thermal conductivity; and
- wide-range equations of state which cover the entire fluid range including the vapor–liquid coexistence curve and the critical region.

With this background, it is the purpose of this paper to present a safe and rapid method for optimizing the functional structure of empirical equations representing a two- or more-dimensional relationship between the variables. The application of this method results in an equation which meets the quality requirement for representing the experimental data with the lowest number of fitted coefficients.

Since we are engaged in the field of very accurate wide-range equations of state for pure substances, we refer mainly to this example but the procedure is not limited to this application.

Considering that the new procedure can be applied to establish any effective correlation equation (the method can also be used for the establishment of correlation equations in connection with any process calculations even if such an equation describes a multidimensional relationship between variables), the method is described in a general way. Only the example given at the end of this paper specifically relates to a vapor pressure equation and an equation of state explicit in the Helmholtz energy.

As a first demonstration of the efficiency of the new procedure, a fundamental equation of state for water has been established by Saul and Wagner [1]. At present, we are using this procedure for establishing a new equation of state for methane [2].

2. BACKGROUND AND PREVIOUS OPTIMIZATION PROCEDURES

The structure of equations of state has ranged from simple cubic equations having 2 [3, 4] to 5 [5] adjusted coefficients over the original Benedict–Webb–Rubin equation [6] with 8 coefficients and its extensions with 20 coefficients [7] up to very complex formulations with about 50 terms [8, 9]. In most cases, these equations of state have not been optimized with respect to their structure. This means that the terms in these equations have been determined subjectively by experience or by trial and error. For the optimization of formulations describing two-dimensional problems such as vapor pressure equations, Wagner [10, 11] developed a special version of a stepwise regression analysis, which has been adapted by de Reuck and Armstrong [12] for the development of equations of state. Based on the knowledge that the regression analysis does not provide sufficient variability to optimize complex problems such as the determination of wide-range fundamental equations of state, Ewers and Wagner [13, 14] developed the evolutionary optimization method (EOM), a random search strategy which uses some principles from biological evolution. This method was used by Schmidt and Wagner [15] for establishing an equation of state for oxygen which was used to calculate the IUPAC tables on oxygen [16].

In our terminology, the optimization of the structure of an empirical equation means the development of effective functional expressions for the description of a relationship between experimental data which consists of the following steps.

(1) Establishing a general functional expression, the bank of terms. Any mathematical function, a_i, which can be considered to be significant for the description of the physical dependency should be included in the bank of terms.

(2) Selecting that combination of terms, a_i, which yields the best description of the physical relationship with a minimum number of terms.

During the last decade two different procedures have been used for the determination of the optimum functional expressions, the stepwise regression analysis [10, 11] and the EOM [13, 14].

The regression analysis developed by Wagner [10, 11] selects the optimum combination of terms a_i using statistical criteria. This method is purely deterministic, it is fast and has been used internationally for years, especially for the establishment of vapor pressure equations [17–23] and

equations of state [21, 24–27] from a bank of terms which did not contain more than 100 terms.

To achieve a greater flexibility which is necessary for the development of effective longer equations of state from a large bank of terms (up to 700 terms), a teachable random search strategy, the evolutionary optimization method (EOM), was developed by Ewers and Wagner [13, 14]. In contrast to the stepwise regression analysis, which determines a single equation out of the bank of terms, the EOM optimizes a population of NP equations simultaneously. As in the biological evolution, the EOM requires a large population and many generations for the determination of the optimum. Therefore it requires a lot of computer time. Another disadvantage is that this method is able to optimize the structure only for a predetermined number of terms in the final equation. Because of its complexity, the EOM has not been used by others.

3. THE NEW OPTIMIZATION METHOD

The new optimization method combines most of the advantages of the regression analysis [10, 11] and the EOM [13, 14] by satisfying the following requirements:

(1) The resulting equation has at least the same quality as an equation determined by using the EOM.

(2) The structure and the length of the equation are optimized simultaneously.

(3) The program consumes much less computer time than the EOM.

3.1. Construction of the Regression Matrix

Before starting the procedure one must formulate a convenient bank of terms. Since the new method requires information on the composition of the bank of terms and on the experimental data in a special form (the so-called regression matrix), the structure of this matrix is presented in detail.

In general, an experimental procedure yields a set of M data points $(\bar{x}, y)_m$ $(m = 1, 2, ..., M)$, where y denotes the dependent variable and $\bar{x}$ represents a vector of independent variables x_k $(k = 1, 2, ..., K)$. Since these data $(\bar{x}, y)_m$ are subject to experimental errors we have to regard the data as estimates of the true values X_k and Y of the unknown physical relationship $\xi(\bar{X}, Y) = 0$. The goal of the empirical procedure for establishing equations is to determine a functional relationship $\zeta(\bar{x}, y, \bar{n})$ by using the experimental data in such a way that this relationship optimally

approximates the unknown physical relation ξ between the variables X_k and Y. This is expressed by[2]

$$\xi(\bar{X}, Y) = 0 \approx \zeta(\bar{x}, y, \bar{n}) \tag{1}$$

where $\bar{n}$ denotes a vector containing the estimates $n_i (i = 1, 2, ..., I)$ for the coefficients of the I terms of the relationship used for the representation of the data set. Numerical estimates of the coefficients can be calculated using the maximum-likelihood method [28–31]. To obtain estimates of the values n_i, one must minimize the weighted sum of squares

$$\chi^2 = \sum_{m=1}^{M} \frac{\zeta(\bar{x}, y, \bar{n})_m^2}{\sigma_m^2} \tag{2}$$

where $\zeta(\bar{x}, y, \bar{n})$ is a relationship between y and x_k in which, as is necessary for the application of our optimization method, the n_i must be linear in this function. A general form of this functional relationship can be expressed as

$$\zeta(\bar{x}, y, \bar{n}) = a_0 - \sum_{i=1}^{I} n_i a_i \tag{3}$$

where

$$a_0 = a_0(\bar{x}, y) \tag{3a}$$

and

$$a_i = a_i(\bar{x}) \tag{3b}$$

The variances σ_m^2 are calculated with the Gaussian error propagation formula

$$\sigma_m^2 = \left(\frac{\partial \zeta}{\partial y}\right)^2 \sigma_{y_m}^2 + \sum_{k=1}^{K} \left(\frac{\partial \zeta}{\partial x_k}\right)^2 \sigma_{x_{k,m}}^2 \Bigg|_{y = y_m,\, x_k = x_{k,m}} \tag{4}$$

where the σ_{y_m} and $\sigma_{x_{k,m}}$ are estimates of the standard deviation of the dependent and independent variables for a data point $(\bar{x}, y)_m$. The partial derivatives $(\partial\zeta/\partial y)$ and $(\partial\zeta/\partial x)$ required for the evaluation of Eq. (4) are determined by using a preliminary equation for $\zeta(\bar{x}, y, \bar{n})$.

For a given bank of terms with I elements, a_i, and M data points, the minimization of χ^2 leads to I normal equations in I unknowns n_i. The jth equation can be represented by

$$\sum_{m=1}^{M} \frac{a_{j,m}}{\sigma_m} \left(\sum_{i=1}^{I} \frac{a_{i,m} n_i}{\sigma_m} \right) = \sum_{m=1}^{M} \frac{a_{o,m} a_{j,m}}{\sigma_m^2} \tag{5}$$

[2] Definitions of symbols are given under Nomenclature (below).

where the coefficients a_i are defined by Eq. (3). This can be represented in matrix notation as

$$[A][N] = [Q] \tag{6}$$

where $[A]$ is a square matrix with a general element

$$a_{ij} = \sum_{m=1}^{M} \frac{a_{i,m} a_{j,m}}{\sigma_m^2} \tag{7}$$

$[N]$ and $[Q]$ are column vectors of the order I, containing the n_i and the right-hand side of Eq. (5), respectively.

Constraints may be included using the method of the Lagrangian multipliers as proposed by Hust and McCarty [32]. If it is required that the function $\zeta(\bar{x}, y, \bar{n})$ fulfills C constraints, the quantity

$$\chi^2 = \sum_{m=1}^{M} \frac{\zeta(\bar{x}, y, \bar{n})_m^2}{\sigma_m^2} + \sum_{c=1}^{C} \lambda_c \zeta(\bar{x}, y, \bar{n})_c \tag{8}$$

must be minimized, where $\zeta(\bar{x}, y, \bar{n})_c$ is the function $\zeta(\bar{x}, y, \bar{n})$ under the condition of the cth constraint (λ_c is the cth Lagrangian multiplier).

The weighted sum of squares χ^2 will be a minimum when the partial derivatives with respect to n_i and λ_c are zero. The minimization with respect to n_i leads to I equations in $I+C$ unknowns. The following kth equation is typical:

$$\sum_{m=1}^{M} \frac{a_{k,m}}{\sigma_m} \left(\sum_{i=1}^{I} \frac{a_{i,m} n_i}{\sigma_m} \right) + \sum_{c=1}^{C} a_{k,c} \lambda_c' = \sum_{m=1}^{M} \frac{a_{o,m} a_{k,m}}{\sigma_m^2} \tag{9}$$

with

$$\lambda_c' = (-\tfrac{1}{2})\, \lambda_c \tag{9a}$$

The derivatives of χ^2 with respect to λ_c yield C linear equations in I unknowns in which the cth equation can be expressed by

$$\sum_{i=1}^{I} n_i a_{i,c} = a_{o,c} \tag{10}$$

($a_{i,c}$ are the elements of the bank of terms under the condition of the constraint).

The combination of I equations of the form according to Eq. (9) and C equations according to Eq. (10) can be written in matrix notation as

$$\begin{bmatrix} [A] & [C] \\ [C]^{\mathrm{T}} & [0] \end{bmatrix} \begin{bmatrix} [N] \\ [\lambda] \end{bmatrix} = \begin{bmatrix} [Q] \\ [QC] \end{bmatrix} \tag{11}$$

where $[C]$ denotes an $I \times C$ matrix that has a general element $a_{i,c}$, $[C]^T$ is the transpose of $[C]$, $[0]$ is a $C \times C$ null matrix, $[\lambda]$ is a column vector of the order C that contains the Lagrangian multipliers λ'_c, and $[QC]$ is a column vector of the order C, where each element is the value of the function a_0 under the condition of the constraint.

From the elements of Eq. (11) and the single element S, which equals χ^2 as defined by Eq. (8), the following coefficient matrix is constructed:

$$[B] = \begin{bmatrix} [A] & [C] & [Q] \\ [C]^T & [0] & [QC] \\ [Q]^T & [QC]^T & [S] \end{bmatrix} \tag{12}$$

where $[B]$ is a symmetric matrix of the order $L = (I + C + 1)$. The new algorithm for the modified stepwise regression analysis needs only one part of the symmetric matrix [B]. In the next section the general elements of $[B]$ are expressed by the notation b_{ij} and $i \geqslant j$. The subscripts i and j refer to the ith row and jth column of the matrix, with $i \geqslant j$ indicating the use of only the lower part of the symmetric matrix $[B]$. The notation b_{LL} refers to the element $[S]$, which always contains the sum of squares χ^2 of the residual between experimental data and the values calculated from the correlation equation considered.[3]

For the purpose of checking whether a term a_i in the bank of terms is included in an equation or not, a column vector $[IN]$ of the order $I + C$ is introduced. Each element of this vector refers to one term a_i in the bank of terms. The value of an element IN_i changes from zero to one at the time when the corresponding term a_i is added to the equation.

3.2. The New Algorithm

Figure 1 presents a flowchart of the new optimization method. Before starting the procedure, according to step 1 in Section 2, one must formulate a convenient bank of terms; cf. Eq. (3). Based on this bank of terms and the experimental data the regression matrix $[B]$ according to Eq. (12) must be calculated.

The optimization process is carried out for a population of NP parameter vectors $\bar{P}_p$ $(p = 1, 2, ..., NP)$, where the number NP has to be predetermined.

The process starts with the establishment of the first set of the NP equations. Each component of a vector $\bar{P}$ represents the position i of a term

[3] Note that in the computer program the lower part of the matrix $[B]$ should be stored in a one-dimensional field. This reduces the computer time significantly and saves computer storage.

a_i in the bank of terms. The N components of each equation are randomly selected from the bank of terms, where N is an estimate of the maximum length which the equation might have. After the selection of the terms, the quality criterion χ^2 is calculated. To achieve reasonable starting points on the optimization surface, it is necessary to repeat this initialization procedure NS times for each equation of the population, yielding NS possible parameter vectors for each equation. Values for the control parameters NP, NS, etc., are given in Table III. From each of the NS attempts the equation with the lowest weighted sum of squares is selected. Those NP equations

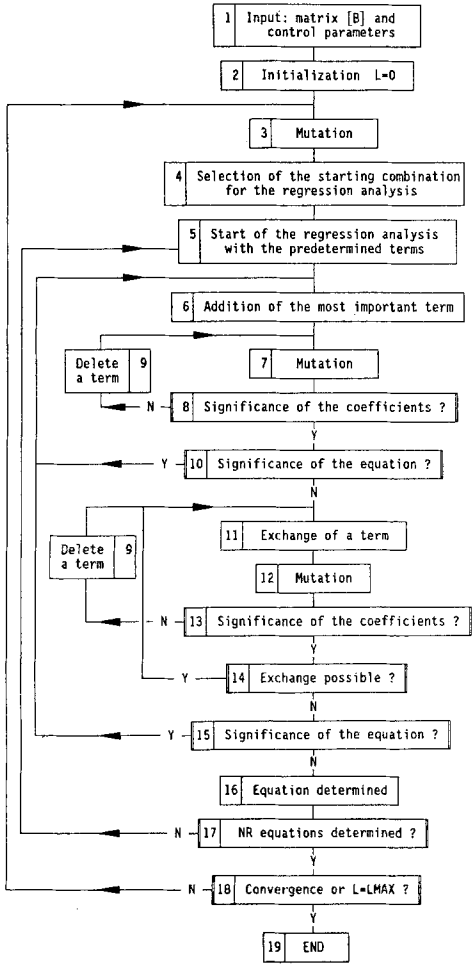

Fig. 1. Flowchart of the new optimization method.

with the smallest sum of squares form the parental generation $L = 0$. This step is called initialization; cf. box 2 in Fig. 1.

The next important step in the new optimization method, the step "mutation," is modeled similarly to a procedure called "mutation" of the EOM [13, 14]. This mutation process is explained in connection with a simple example.

In this example, from a bank of 100 terms, an equation with the terms 5, 9, 30, 45, 60, 70, and 90 has been selected in the initialization step.

For the purpose of improving the quality of the equation (parameter vector) by mutation, the following procedure is applied.

(1) A random selection of a limited number of components $p_{n,\text{old}}$ of the actual parameter vector $\bar{P}$ is made. The number of terms which have to be exchanged should not exceed $N/2$.
For this example, the random number generator might determine that the terms 5, 30, 70 of the equation have to be replaced.

(2) New values for these selected components $p_{n,\text{old}}$ are determined by alternately using the following two steps:

(a) $$p_n = p_{n,\text{old}} + z(0, \sigma) \tag{13}$$

$z(0, \sigma)$ are normally distributed random numbers with the expected value 0 and a standard deviation σ. In general, the normally distributed random numbers should cover a range from -3 to $+3$.
In the example, the term $p_{n,\text{old}} = 5$ is replaced by $p_n = 7$ if the random number generator yields $z(0, \sigma) = +2$ for this exchange.

(b) No restrictions are imposed on the selection of the new values p_n except the condition

$$1 \leqslant p_n \leqslant \text{I} \qquad \text{and} \qquad p_n \neq p_{\text{old},j} \qquad (j = 1, 2, \ldots, N)$$

which means that the new value of p_n indicates any element in the bank of terms which has not yet been an element of the equation.
In the example, $p_{n,\text{old}} = 30$ might be replaced by the element $p_n = 98$.

In the example, $p_{n,\text{old}} = 70$ is replaced by $p_n = 69$, using again the procedure described under step a). In this case $z(0, \sigma)$ was -1.

(3) The quality determination is carried out by fitting the actual equation to the data.

In the example, the sum of squares χ^2_{new} for the mutant with the terms 7, 9, 45, 60, 69, 90, and 98 is determined.

(4) If $\chi^2_{new} \leqslant \chi^2_{old}$ the old equation is replaced by the mutant.

This procedure is applied NM times to each equation at different steps during the optimization cycle; cf. boxes 3, 7, and 12 in Fig. 1.

Now there are NP equations which represent NP different points on the optimization surface. Although these equations might have different structures and qualities, there are always some elements a_i which are present in several of the NP equations in the population. In general, these are the terms which are most important for the description of the physical connection considered. With the assumption that an equation with a small sum of squares (higher quality) contains more of these important terms than an equation with a high sum of squares (lower quality), only $NR+1$

Table I. Transformation of Matrix $[B]$ for the Addition and Deletion of a Term Denoted by the Subscript k[a]

Transformation	Condition
$b_{ij} = \frac{1}{b_{kk}}$	(1) $i=j=k$
$b_{ij} = \frac{b_{ij}}{b_{kk}}$	(2) $i=k,\ j<k$ or $j=k,\ i>k$
$b_{ij} = b_{ij} + \frac{b_{ik}^2}{b_{kk}}(-1)^{c+IN(i)}$	(3) $i=j>k$
$b_{ij} = b_{ij} + \frac{b_{ki}^2}{b_{kk}}(-1)^{c+IN(i)}$	(4) $i=j<k$
$b_{ij} = b_{ij} + \frac{b_{ik}b_{jk}}{b_{kk}}(-1)^{c}$	(5) $i>k,\ j>k,\ i\neq j$
$b_{ij} = b_{ij} + \frac{b_{ik}b_{kj}}{b_{kk}}(-1)^{c}$	(6) $i>k,\ j<k,\ i\neq j$
$b_{ij} = b_{ij} + \frac{b_{ki}b_{kj}}{b_{kk}}(-1)^{c}$	(7) $i<k,\ j<k,\ i\neq j$
$1 \leqslant i \leqslant L, \quad 1 \leqslant j \leqslant L, \quad i \geqslant j$	

[a] The difference between the addition and the deletion of a term in the algorithm is

addition: $c=1$

deletion: $c=2$

The element b_{LL} is treated as a normal element using condition (3) with $IN(L)=0$.

equations of the NP equations of the population are compared to determine the most important terms. Therefore, in the next optimization step, "selection of the starting combination for the regression analysis" (cf. box 4) such terms, a_i, are determined which appear $NR+1$, NR,..., 2 times in the $NR+1$ equations with the highest quality out of the NP equations of the population ($NP=5$ and $NR=3$ might be examples for these control parameters; cf. Table III).

The next step in the optimization process is the application of the modified stepwise regression analysis. The regression matrix $[B]$ already introduced provides the necessary information for the procedure. The algorithm for the stepwise transformation of the regression matrix presented here is a modification of the procedure introduced by Wagner [10, 11]. The new algorithm allows the calculation of the coefficients, the standard deviation of the coefficients, and other statistical values using only half of the matrix [B]. Efroymson [33], Draper and Smith [34], and de Reuck and Armstrong [12] presented similar methods for the transformation of the matrix, but in general their algorithms require more computer storage capacity. The first regression run starts with incorporating those terms into the regression equation which appear simultaneously in the best $NR+1$ equations of the generation. These terms are added to the equation using the algorithm presented in Table I. The necessary operations for the computation of new elements are given in the first column in Table I. The condition in the second column locates the elements in matrix [B]. After the addition of the preselected terms, the element b_{LL} of the matrix contains the sum of squares, i.e., the quality criterion for the equation.

In the next step (cf. box 6 in Fig. 1), it is necessary to determine that term which should be included next. The procedure uses the relation

$$\chi_n^2 = b_{n,\mathrm{LL}} = b_{o,\mathrm{LL}} - \frac{b_{\mathrm{L}i} b_{\mathrm{L}i}}{b_{ii}} \tag{14}$$

to examine the effect of adding a further term a_i to the regression equation. The subscripts n and o refer to the new and old sum of squares, respectively, and L equals $I+C+1$, which indicates the bottom line in the matrix $[B]$. The term which reduces χ^2 by the greatest amount is then selected for inclusion into the correlation equation and is added to the equation using the algorithm presented in Table I.

After adding the next term the mutation cycle described previously is repeated NM times; cf. box 7. The calculation of the quality criterion of the mutants is not done by adding and deleting terms from the actual equation using the algorithm in Table I, because this would require too many transformations of the matrix $[B]$. Instead of transforming the regression matrix, the following procedure is applied.

(1) At the beginning of the optimization process the original matrix $[B]$ is copied onto a matrix $[BB]$, the working matrix.

(2) The appropriate elements, b_{ij}, of the working matrix $[BB]$ are selected for the construction of a system of normal equations similar to Eq. (11).

(3) These equations are solved for the coefficients n_i by the use of standard procedures for the evaluation of linear systems of equations.

If any of the proposed mutants indicates a reduction in χ^2, then the regression equation is replaced by the mutant. This requires the transformation of matrix $[B]$ using the algorithm in Table I for adding and deleting terms.

After each transformation of the regression matrix, statistical tests on the coefficients and on the equation as a whole are carried out. At first, the statistical probability that each coefficient n_i which is already in the equation differs from zero is tested by the Student t test. The standard deviation of each coefficient n_i already in the equation is given by

$$\sigma_{n_i} = [b_{LL} b_{ii}/(M - N_a)]^{1/2} \tag{15}$$

where M corresponds to the number of data points and N_a refers to the number of terms in the actual equation at that time. For a coefficient n_i, the Student t statistic is given by

$$t_i = \frac{n_i - \beta_i}{\sigma_{n_i}} \tag{16}$$

where the value of n_i is given by the element b_{Li} of the matrix $[B]$.

The probability, S_i, that the coefficient n_i differs from zero ($\beta_i = 0$) is expressed by the statistical probability of the Student t distribution,

$$S_i = (1/\sqrt{\pi\nu}) \left[\Gamma\left(\frac{\nu+1}{2}\right) \Big/ \Gamma\left(\frac{\nu}{2}\right) \right] \int_{-t_i}^{t_i} \left(1 + \frac{t^2}{\nu}\right)^{-(\nu+1)/2} dt \tag{17}$$

where Γ is the gamma function and ν defines the number of degrees of freedom $\nu = (M - N_a)$. Equation (17) can be evaluated using a procedure from a convenient statistical computer package.

The comparison of the value S_i and any value, P_t, between zero and unity specified by the correlator (cf. Table III) yields the criterion for the rejection of a term. If the S_i value for any of the coefficients n_i falls below the chosen value P_t, the term a_i related to the coefficient n_i with the minimum value S_i is removed from the actual equation using the algorithm in

Table I, i.e., the hypothesis that the coefficient n_i is zero is accepted. This step is repeated until all values S_i exceed the assigned value P_t. A problem may occur if the term which has to be removed corresponds to the last term added to the equation. Such an elimination would result in an endless exchange of that term. To avoid this problem, the optimization step "exchange of a term" (cf. box 11) is applied in that case. This is explained in detail below.

Since the equation has to be optimized in structure *and* length, it is necessary to apply a second statistical test which should indicate whether the equation has reached its optimum number of terms. The variance V of the equation as a whole is given by

$$V = b_{\mathrm{LL}}/(M - N_a) \tag{18}$$

and the relation

$$V_{-1} = \left(b_{\mathrm{LL}} + \frac{b_{\mathrm{L}i} b_{\mathrm{L}_i}}{b_{ii}}\right) \Big/ (M - N_a + 1) \tag{19}$$

allows the calculation of the variance V_{-1} of the equation without the term a_i, which has the minimum probability S_i that its coefficient n_i differs from zero. The statistical probability of the Fisher F distribution is calculated using the equation

$$S = \left[\Gamma\left(\frac{\nu_{-1} + \nu}{2}\right) \Big/ \Gamma\left(\frac{\nu_{-1}}{2}\right) \Gamma\left(\frac{\nu}{2}\right)\right] (\nu_{-1})^{\nu_{-1}/2}\, \nu^{\nu/2}$$
$$\times \int_0^F \left[f^{(\nu_{-1}-2)/2} / (\nu + \nu_{-1} f)^{(\nu_{-1}+\nu)/2}\right] df \tag{20}$$

where ν is the number of degrees of freedom of the actual equation, $M - N_a$, ν_{-1} is the number of degrees of freedom of the equation with the rejected term $M - N_a + 1$, and the Fisher F statistic is defined by

$$F = V_{-1}/V \tag{21}$$

Like Eq. (17), Eq. (20) can also be evaluated using a procedure from a convenient statistical computer package. Equation (20) provides a test of significance between the two estimates of the variances. If the computed value, S, falls below an assigned value P_{F}, this is an indication either that the inclusion of the term with the minimum S_i value is not justified and that the final equation must contain $N_a - 1$ terms or that an intercorrelation between several terms occurs.

The decision whether this F test failed because of intercorrelations

between several terms of the regression equation or because the equation has reached its final length is made by the optimization step "exchange of a term" (cf. box 11).

In order to remove the effect of intercorrelation between terms, the possibility of the exchange of a term from the equation with any term from the bank of terms is considered. Each term in the equation, except the last one added, is exchanged in turn with all remaining terms in the bank of terms. Since the effect on the sum of squares by each of the proposed exchanges is calculated using the algorithm in Table II, it is not necessary to transform the matrix $[B]$.

Such an exchange which indicates the greatest reduction of the sum of squares is carried out by eliminating the appropriate term a_n from the equation and adding the term a_m. After the exchange of terms and the application of the procedure to the random variation of the equation (see box 12), the test on the significance of the coefficients is repeated. If the equation contains a nonsignificant coefficient, the corresponding term is deleted and the optimization process is continued with the step "exchange of terms." If the t test shows that all coefficients are significant, then the exchange of terms is continued until no further reduction of the sum of squares can be achieved.

After the completion of this optimization step, the significance of the equation as a whole is tested. If this test is passed, the procedure continues with the addition of a new term; cf. box 6. The regression run is completed, i.e., the equation has reached the optimum length, if no significant reduc-

Table II. Calculation of the Sum of Squares χ^2_{mn} of an Equation in Which the Term n Is Exchanged for a Term m from the Bank of Terms Which Has Not Yet Been in the Equation

Condition	
$m > n$	$m < n$
$c_m = b_{Lm} + \frac{b_{Ln} b_{mn}}{b_{nn}}$	$c_m = b_{Lm} + \frac{b_{Ln} b_{nm}}{b_{nn}}$
$d_m = b_{mm} + \frac{b_{mn}^2}{b_{nn}}$	$d_m = b_{mm} + \frac{b_{nm}^2}{b_{nn}}$
$SS = b_{LL} + \frac{b_{Ln}^2}{b_{nn}}$	
$\chi^2_{mn} = SS - \frac{c_m^2}{d_m}$	

tion of the sum of squares is achievable, either by the addition of a term or by the exchange of terms.

After the optimization of the first regression equation has been completed, the modified stepwise regression analysis is started again until NR equations are determined, e.g., the second regression equation is optimized starting with those terms which occur NR times in the $NR+1$ equations with the minimum sum of squares of the parental generation.

3.3. Constraints

The treatment of constraints is similar to that of adding terms to the equation. As, initially, the original matrix $[B]$ contains zero elements on its main diagonal, it is not possible to add the constraints at the beginning of a regression run. Therefore, the following procedure is applied. In each regression run the equation is optimized to its final length. Then as many terms as there are constraints are removed from the regression equation. The constraints are added using the algorithm of Table I with the restriction that the terms related to the constraints cannot be deleted from the equation during the regression run. After including the constraints, the optimization is continued in box 6 following the normal procedure.

3.4. Convergence Criterion, Control Parameters, and Applications

The first optimization cycle is completed after the determination of NR regression equations and the new parental generation is established by replacing the NR equations with the lowest quality of the old parental generation with the NR regression equations. It is important that each regression equation enters the population of the next generation even if it will not immediately lead to an improvement of the global quality of the generation. Since a difference in the quality of equations implies a difference of the structure (terms a_i) of these equations, the incorporation of regression equations with lower quality into the new generation effects the optimization step, "selection of the starting combination for the regression analysis," of the new generation. The use of the new starting terms for the next modified stepwise regression analysis may produce equations with a smaller sum of squares. Therefore, it is necessary that regression equations of lower quality enter the next generation. Based on this optimization feature, local optima which might be dead ends of the optimization process can be avoided. The whole optimization process is completed if the test of convergence (cf. box 18) indicates that all equations of a generation are identical or that a predetermined number of cycles has been reached.

The optimization of functional structures of different thermodynamic

Table III. Proposed Values of the Control Parameters for Different Optimization Problems

Characterization of the problem		I	II	III
Maximum number of terms in an eq.	N	$\leqslant 10$	$\leqslant 30$	$\leqslant 60$
Elements in the bank of terms	I	$\leqslant 200$	$\leqslant 400$	$\leqslant 700$
Control parameters		I	II	III
Number of eqs. in a generation	NP	5	4	3
Number of regression runs in each generation	NR	3	2	2
Number of start attempts for the initialization	NS	60	60	60
Number of mutations	NM	60	60	60
Probability value for the t test	P_t	0.9999	0.9999	0.9999
Probability value for the F test	P_F	0.9999	0.75	0.6

problems, ranging from equations for the melting pressure [35] over equations for the vapor pressure and orthobaric densities [36] and equations of state [1, 2] to correlation equations for the transport properties of oxygen [37], has verified the universal applicability of the new optimization method. It became obvious that all problems studied could be divided into three categories. These cases differ in the expected length of the equation and the number of elements in the bank of terms. Table III summarizes these categories and proposes values for the control parameters for all the problems considered.

4. EXAMPLES

Two examples are given in this section. First, the application of the new optimization procedure is shown by the example of the establishment of an effective vapor pressure equation. The second example demonstrates how the complex problem of an equation of state in the form of a fundamental equation for the Helmholtz energy can be combined with the very general Eqs. (2) to (4).

4.1. Establishing a Vapor Pressure Equation

It is demonstrated how the new optimization procedure finds an optimized structure of a vapor pressure equation which represents a given set of 161 experimental vapor pressures of methane. The data and their experimental uncertainties were taken from a paper published by Kleinrahm and Wagner [20].

When establishing a vapor pressure equation, the first step is to formulate a comprehensive bank of terms. For this purpose, the following general bank of terms has proven to be very effective [10, 11, 17, 19–21, 23]:

$$\ln(p/p_c) = (T_c/T) \sum_{i=1}^{I} n_i (1 - T/T_c)^{i/2} \tag{22}$$

where p denotes the vapor pressure, T the temperature, and T_c and p_c are the critical temperature and pressure, respectively. With $I = 21$, the bank of terms contains 21 elements.

If this example is combined with the general Eq. (3), then $\bar{x}$ and y correspond to T/T_c and $\ln(p/p_c)$, respectively. Furthermore, it is

$$a_0 = \ln(p/p_c)(T/T_c) \tag{23a}$$

$$a_i = (1 - T/T_c)^{i/2} \qquad \text{for} \quad i = 1, 2, \ldots, 21 \tag{23b}$$

This example belongs to the first category of optimization problems given in Table III and the control parameters proposed for that category are applied. To present the complete optimization run in a single figure we used $NP = 4$ and $NR = 2$ instead of the values given in Table III. In addition to that, the maximum number of terms N in the equation is set to four. Figure 2 presents the structure of the equations together with their weighted sum of squares χ^2 at the most important optimization steps. The structure of each equation is characterized by the position, i, of the corresponding term, a_i, in the bank of terms.

The optimization starts with the random selection of four equations. For each of the four equations 60 attempts are made to select its four terms. From each of the 60 attempts the equation with the lowest weighted sum of squares is selected. As a result of this initialization (cf. box 2 in Fig. 1), these four equations form the parental generation $L = 0$. After completing the initialization the optimization step "mutation" is applied to each equation of the parental generation. This results in a set of equations with a higher quality than that of the parental generation. By comparing the structure of the three equations ($NR + 1 = 3$) with the smallest weighted sum of squares, those terms are determined which appear in two or in three equations at this optimization step. Now two regression runs are started. The first regression run starts with the addition of the terms which appear in $NR + 1$ equations, here the terms 2 and 3. In the second run the terms 6 and 16 are added first to the regression equation. As a result of the optimization step "regression analysis," two equations are formed. The next generation ($L = 1$) is established in such a way that the two worst equa-

tions of the old parental generation are replaced by the two regression equations. Now the new generation contains equations which have, on average, a better quality than those of the generation $L = 0$. The optimization cycle continues with the step "mutation" (box 3 in Fig. 1). This cycle is repeated until the convergence criterion is met or $L = \text{LMAX}$. It can be seen that all equations of the generation $L = 3$ have an identical form, and the convergence criterion is fulfilled. This final equation is identical with the

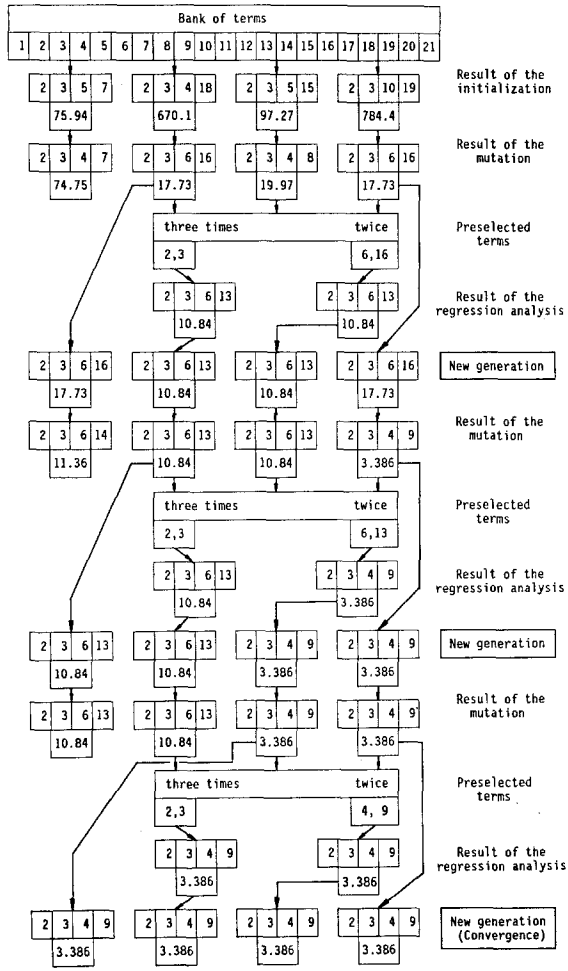

Fig. 2. Example of the determination of a vapor pressure equation with the new optimization procedure.

vapor pressure equation given by Kleinrahm and Wagner [20] which was determined with the EOM.

The application of the old stepwise regression analysis developed by Wagner [10, 11] which uses the same statistical criteria (P_t, P_F) results in an equation with the terms 2, 3, 6, and 13. This demonstrates that even simple optimization problems are not always satisfactorily solved using the stepwise regression analysis.

4.2. The Equation of State Explicit in the Helmholtz Energy

The second example comes from the field of accurate wide-range equations of state. Since recent forms of these equations are fundamental equations for the Helmholtz energy, A, such a form is also used here. However, the application of the general Eq. (3) to a function explicit in the Helmholtz energy is relatively complex because the function to be minimized with respect to the coefficients, n_i, contains not only the terms of the general function itself but also the derivatives with respect to density or temperature depending on the property considered. Therefore, the application of Eq. (3) when fitting a Helmholtz energy equation to two selected thermodynamic properties ($p\rho T$ data, c_v data) is shown as follows.

The dimensionless Helmholtz energy $\Phi = A/(RT)$ is commonly separated into a part depending on the ideal gas behavior Φ^0 and a part which takes into account the real fluid behavior Φ^r, namely,

$$\Phi(\delta, \tau) = \Phi^0(\delta, \tau) + \Phi^r(\delta, \tau) \tag{24}$$

where $\delta = \rho/\rho_c$ is the reduced density and $\tau = T_c/T$ is the inverse reduced temperature, with ρ_c and T_c as the critical density and critical temperature, respectively. The equation for $\Phi^0(\delta, \tau)$ can be obtained from a correlation equation for the isobaric heat capacity in the ideal-gas state (cf. Wagner and de Reuck [16] and Saul and Wagner [1]).

Again, the first step is to define the bank of terms for $\Phi^r(\delta, \tau)$. For reasons of simplicity the bank of terms is expressed as a polynomial of δ and τ, although, in reality, an effective form of such a bank of terms should also contain exponential functions of the type $\exp(-\delta^i)$ ($i = 1, 2, ..., 6$) combined with polynomials in δ and τ; for details see Schmidt and Wagner [15], Jahangiri et al. [21], and Saul and Wagner [1]. With this restriction, the bank of terms for Φ^r can be written as

$$\Phi^r(\delta, \tau) = \sum_{j=1}^{15} \sum_{k=1}^{10} n_{jk} \delta^j \tau^k \tag{25}$$

This arbitrarily chosen bank of terms for the real part of the Helmholtz energy contains 150 terms. Since the Helmholtz energy is not

accessible to direct measurements, it is necessary to determine the coefficients n_{jk} in any expression for Φ^r which is a subsum of Eq. (25) by using such thermodynamic properties which are experimentally available.

The use of more than only one thermodynamic property is called "multiproperty fitting," which is the state-of-the-art procedure for establishing effective wide-range equations of state. The optimization procedure can be directly applied only if the χ^2 depends linearly on the coefficients n_i; cf. the comment on Eq. (2). This means, transferred to the example given here, that only such thermodynamic properties can be considered which depend on $\Phi^r(\delta, \tau)$ and/or its derivatives in a linear way. This is valid only for $p\rho T$ data, the condition for the phase equilibria between the vapor and the liquid phase (Maxwell criterion), second and third virial coefficients, isochoric heat capacities, and internal energies; cf. Ahrendts and Baehr [30, 31] and Saul and Wagner [1]. To avoid too much complexity the used properties are limited to $p\rho T$ data and isochoric heat capacities $c_v(\rho, T)$. Their relation to the real part of the Helmholtz energy is given by

$$p = \rho RT(1 + \delta\Phi^r_\delta) \tag{26}$$

$$c_v/R = -\tau^2(\Phi^0_{\tau\tau} + \Phi^r_{\tau\tau}) \tag{27}$$

where R is the gas constant and the abbreviations of the partial derivatives of Φ^0 and Φ^r are defined by

$$\Phi^r_\delta = (\partial\Phi^r/\partial\delta)_\tau; \qquad \Phi^r_{\tau\tau} = (\partial^2\Phi^r/\partial\tau^2)_\delta; \qquad \Phi^0_{\tau\tau} = (\partial^2\Phi^0/\partial\tau^2)_\delta \tag{28}$$

Based on Eqs. (25) to (28), the general equations (2) and (3) can be specified as

$$\zeta_1[\varphi(\Phi^r), p_m, T_m, \rho_m] = a_{0,1} - \sum_{j=1}^{15}\sum_{k=1}^{10} n_{jk} a_{jk,1} \tag{29}$$

with

$$a_{0,1} = [p_m/(\rho_m RT_m) - 1]/\delta_m \tag{29a}$$

$$a_{jk,1} = \Phi^r_\delta = (j)\,\delta_m^{j-1}\tau_m^k \tag{29b}$$

and

$$\zeta_2[\varphi(\Phi^r), c_{v,m}, T_m, \rho_m] = a_{0,2} - \sum_{j=1}^{15}\sum_{k=1}^{10} n_{jk} a_{jk,2} \tag{30}$$

with

$$a_{0,2} = c_{v,m}/R + \tau^2\Phi^0_{\tau\tau} = [c_{v,m} - c^0_v(T_m)]/R \tag{30a}$$

$$a_{jk,2} = -\tau_m^2\Phi^r_{\tau\tau} = -\tau_m^2 k(k-1)\,\delta_m^j\tau_m^{k-2} \tag{30b}$$

where the subscript m denotes experimental information, $c_v^0(T_m)$ is the isochoric ideal-gas heat capacity at a temperature T_m, and $\varphi(\Phi^r)$ indicates that the residuals ζ_1 and ζ_2 depend on the function Φ^r and its derivatives. It can be seen that both residuals $\zeta_1[\varphi(\Phi^r), p_m, T_m, \rho_m]$ and $\zeta_2[\varphi(\Phi^r), c_{v,m}, T_m, \rho_m]$ are linear with respect to the unknown coefficients n_{jk}. The corresponding two sums of weighted squares are expressed by

$$\chi_1^2 = \sum_{m=1}^{M_1} \{\zeta_1[\varphi(\Phi^r), p_m, T_m, \rho_m]\}^2/\sigma_{1,m}^2 \tag{31a}$$

$$\chi_2^2 = \sum_{m=1}^{M_2} \{\zeta_2[\varphi(\Phi^r), c_{v,m}, T_m, \rho_m]\}^2/\sigma_{2,m}^2 \tag{31b}$$

and the coefficients n_{jk} are determined by minimizing the sum

$$\chi^2 = \chi_1^2 + \chi_2^2 \tag{32}$$

To complete the picture, the fact should be emphasized that many thermodynamic properties (speed of sound, isobaric heat capacity, etc.) depend nonlinearly on Φ^r and/or its derivatives. If such "nonlinear" properties are to be taken into account when optimizing the structure of a fundamental equation of the Helmholtz energy, then an iterative procedure of linearization can be applied. This was done in establishing the new equation of state for water [1].

5. CONCLUSION

Based on the shortcomings of the known optimization methods, especially in the determination of equations of state, a new procedure for the optimization of functional structure of thermodynamic correlation equations has been developed. The combining of the most effective elements of the evolutionary optimization method and the stepwise regression analysis into a new concept allows the optimization of functional structures for all problems accessible to the linear-least squares technique. Furthermore, the algorithms given for the transformation of the regression matrix should be incorporated into existing stepwise regression procedures, allowing the optimization to begin from a larger bank of terms with the same amount of computer memory.

Up to now, the new optimization procedure has been successfully applied to the establishment of vapor pressure equations, equations for the densities of the saturated liquid and vapor, wide-range equations of state, and wide-range correlation equations for transport properties.

NOMENCLATURE

A	Helmholtz energy
$[A]$	Matrix
a_i	Element of the bank of terms
$[B]$	Regression matrix
$[BB]$	Working matrix
b_{ij}	Element of the matrix $[B]$
C	Number of constraints
$[C]$	Matrix containing constraints
c, i, k, m, n, p	Serial numbers
F	Fisher F statistic
I	Number of elements in the bank of terms
K	Number of independent variables
L	Order of the matrix [B]
$[IN]$	Vector
M	Number of experimental data
N	Maximum number of terms in an equation
N_a	Number of terms in an equation
NM	Number of mutations
NP	Number of equations of the population
NR	Number of regression runs in each generation
NS	Number of start attempts for the initialization
$[N]$	Column matrix of coefficients n_i
n_i	Adjustable coefficient
P_F, P_t, S	Statistical probabilities
p	Pressure
p_n	Position of a term in the bank of terms
p_s	Vapor pressure
$[Q], [QC]$	Column matrices
R	Gas constant
S	Weighted sum of squares
T	Temperature
t	Student t statistic
V, V_{-1}	Variance of an equation
X_k	"True" independent state variable
x_k	Independent state variable
Y	"True" dependent state variable
y	Dependent state variable
z	Normally distributed random number
$[0]$	Null matrix
χ^2	Weigted sum of squares

$\delta = \rho/\rho_c$	Reduced density
Γ	Gamma function
λ, λ'	Lagrangian multipliers
ν	Degrees of freedom
ρ	Density
$\Phi = A/(RT)$	Dimensionless Helmholtz energy
σ	Standard deviation
σ^2	Variance
$\tau = T_c/T$	Inverse reduced temperature
ξ	State function
ζ	Empirical relationship

Subscripts

c	Constraint, critical
i, j, k, m, n	Indices for terms in the matrices
n	New
o	Old

Superscripts

r	Real part
T	Transpose of the matrix
$-$	Sign for a vector
$\circ$	Ideal-gas state

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