Calculation of the error in equilibrium constants obtained from tabulated data

E B Rudnyi
Lomonosov Moscow State University

ABSTRACT. We show that in order to obtain a reliable estimate of the error in equilibrium constants the covariances between the enthalpies of formation and the reduced free energies must be used in addition to the errors in the enthalpies of formation and in the reduced Gibbs free energies found in thermodynamic tabulations. By discussing two examples (the compilation only of calorimetric data and only of equilibrium data) we show that the required covariances can be obtained in the course of the normal processing of experimental data.

Increasing numbers of calculations of the equilibrium composition of multicomponent systems are now being published. The precision of these calculations is strongly dependent on the precision of the equilibrium constants used in the calculation (or of the Gibbs free energy $\Delta G° = -RT \ln K°$). Unfortunately, even when the best thermodynamics handbooks[1,2] are used a reliable estimate of the error in the calculated equilibrium constants cannot be obtained.

For example, let us use the handbook Thermodynamic Properties of Pure Substances,[1] which contains the most complete information on the errors of the tabulated thermodynamic quantities, and calculate the error in the equilibrium constant of the reaction

$$KBO_2(s) = KBO_2(g) \qquad (1)$$

at 1100 K. According to the error propagation law we can write

$$R^2 D[\text{Ln } K°(1)] = \frac{1}{T^2} D[\Delta_f H°(g)] + \frac{1}{T^2} D[\Delta_f H°(s)] +$$
$$+ D[\Phi°(g)] + D[\Phi°(s)], \qquad (2)$$

where D is the dispersion. Using the errors in the enthalpies of formation $\{\Delta_f H_0°(KBO_2, s) = -978 \pm 5 \text{ kJ mol}^{-1}, \Delta_f H_0°(KBO_2, g) = -665 \pm 16 \text{ kJ mol}^{-1}\}$ and in the reduced Gibbs free energies $\{\Phi_{1100}°(KBO_2, s) = 117 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}, \Phi_{1100}°(KBO_2, g) = 322 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}\}$ from the handbook[1] the error in the equilibrium constant $\ln K°(1)$ is found to be ± 2.3. This means that the error in the equilibrium constant $K°(1)$ is an order of magnitude, or 1000%.

Yet, the same handbook[1] states that the equilibrium contants of reaction (1) have been measured experimentally at 1050—1230 K, and that in reality their error is less than 50% $\{\pm 0.4 \text{ in } \ln K°\}$.

It is not difficult to see why formula (2) seriously overestimated the error in $K°(1)$ in this case. Glushko et al.[1] obtained the enthalpy of formation $\Delta_f H_0°(KBO_2, g)$ from the experimentally measured equilibrium constants of reaction (1):

$$\Delta_f H°(g) = \Delta_f H°(s) + T[\Phi°(g) - \Phi°(s) - R \ln K°(1)],$$

and used the law of propagation of errors to estimate its error,

$$D[\Delta_f H°(g)] = D[\Delta_f H°(s)] + T^2\{D[\Phi°(g)] + D[\Phi°(s)] + R^2 D[\ln K°(1)]\}.$$

Thus the error in the enthalpy of formation of KBO_2 in the gas phase quoted in the handbook[1] is correlated with the errors in the enthalpy of formation $\Delta_f H°(s)$ and in the reduced Gibbs free energy. This correlation is responsible for the seriously overestimated error in $\ln K°(1)$ when formula (2) is used. It should be noted that the correlation of the errors in the tabulated thermodynamic quantities is a feature common to all thermodynamic handbooks.

In the present case, because the recommendations on the choice of thermodynamic values are argued in depth,[1] the error in the equilibrium constant can be estimated to within (at least) the nearest order of magnitude.

The aim of the present work was to formalise the solution of this problem in the general case. Firstly, we shall identify the information required, in additon to the errors in the thermodynamic quantities, in order to allow for the correlations between the errors. Secondly (and equally important) we shall consider how this information can be obtained from the set of recommended thermodynamic quantities.

Allowance for the correlation between the errors in the enthalpies of formation and in the reduced Gibbs free energies. We shall begin by listing some useful relationships from mathematical statistics[3] which will be used in our discussion. Let **x** be a vector of random quantities, and $\mathscr{D}(\mathbf{x})$ be its dispersion matrix. If **x** consists of independent random quantities, $\mathscr{D}(\mathbf{x})$ has a diagonal form and consists of the individual dispersions of the random quantities. When the random quantities in **x** are mutually correlated the nondiagonal terms in $\mathscr{D}(\mathbf{x})$, called the covariances, are non-zero.

Let the vector of random quantities **y** be a linear transformation of the vector **x**:

$$\mathbf{y} = \mathscr{A}\mathbf{x}$$

(where $\mathscr{A}$ is the transformation matrix). In this case the dispersion matrix of the vector **y** can be calculated by the formula

$$\mathscr{D}(\mathbf{y}) = \mathscr{A}D(\mathbf{x})\mathscr{A}', \qquad (3)$$

where the prime $(')$ denotes transposition. Eqn. (3) is a generalised version of the error distribution law. Formulae like (2) are obtained from (3) only when the random quantities appearing in **x** are linearly independent. Otherwise Eqn. (2) should include the covariances, i.e. the nondiagonal terms from $\mathscr{D}(\mathbf{x})$.

The random quantities which appear in the vector **y** are correlated with the random quantities in the vector **x**. The covariances between the individual random quantities are contained in the covariance matrix cov (**y**, **x**), which can be calculated as follows:

$$\text{cov}(\mathbf{y}, \mathbf{x}) = \text{cov}(\mathbf{x}, \mathbf{y})' = \mathscr{A}\mathscr{D}(\mathbf{x}). \qquad (4)$$

Let us apply Eqn. (3) to the chemical reaction

$$\sum_i \nu_i A_i = 0, \qquad (5)$$

which is defined by the stoichiometric vector $\mathbf{v} = \{v_1, \ldots, v_m\}'$ ($v_i > 0$ for the products and $v_i < 0$ for the reactants). The equilibrium constant $K°(5)$,

$$R \ln K°(5) = -\mathbf{v}'\Delta_f H/T + \mathbf{v}'\Phi,$$

depends on the vectors of the enthalpies of formation, $\Delta_f H = \{\Delta_f H_1^o, \ldots, \Delta_f H_m^o\}'$, and of the reduced Gibbs free energies, $\Phi = \{\Phi_1^o, \ldots, \Phi_m^o\}'$. In our case y is the scalar parameter $R \ln K^o(5)$ and x is the compound vector

$$x = \left[\begin{array}{c} \Delta_t H \\ \Phi \end{array} \right],$$

whose dispersion matrix is

$$\mathcal{D}(x) = \left[\begin{array}{cc} \mathcal{D}(\Delta_t H) & \text{cov}(\Delta_t H, \Phi) \\ \text{cov}(\Phi, \Delta_t H) & \mathcal{D}(\Phi) \end{array} \right],$$

and the transformation matrix $\mathcal{A}$ is the row

$$\mathcal{A} = \left(-\frac{v}{T}, v \right). \qquad G$$

By using Eqn. (3) we obtain the following formula for the dispersion of the equilibrium constant

$$R^2 D\{\ln K^o(5)\} = \frac{1}{T^2}\{v'\mathcal{D}(\Delta_t H)v\} + v'\mathcal{D}(\Phi)v - $$
$$ - \frac{1}{T}\{v'\,\text{cov}(\Delta_t H, \Phi)v + v'\,\text{cov}(\Phi, \Delta_t H)v\}.$$

This equation shows that in order to calculate the error of the equilibrium constant we must know, in addition to the errors in the enthalpies of formation and in the reduced Gibbs free energies [the diagonal terms $\mathcal{D}(\Delta_f H)$ and $\mathcal{D}(\Phi)$], also the covariances between enthalpies of formation [the nondiagonal terms $\mathcal{D}(\Delta_f H)$, the covariances between the reduced Gibbs free energies [the nondiagonal terms $\mathcal{D}(\Phi)$], and the covariances between the enthalpies of formation and the reduced Gibbs free energies [the cov $(\Delta_f H, \Phi)$ matrix]. The use of formula (2) is legitimate only when all these covariances are zero (a very rare case in thermodynamic practice).

Only the errors in the enthalpies of formation and in the reduced Gibbs free energies are quoted in thermodynamics handbooks and original publications at present. The covariances between thermodynamic parameters are not given, and often not even mentioned. The main reason is the lack of familiarity of the majority of experimenters with the concept of covariance. Yet, in the processing of the experimental data the covariances of the parameters are no more difficult to obtain than the errors in the parameters. The following approach can be used. We express the tabulated thermodynamic quantities (vector y) as a function of the experimentally measured values (vector x). Usually the measured quantities are not mutually correlated [$\mathcal{D}(x)$ has a diagonal form]. In the limit the structure of $\mathcal{D}(x)$ can be established by *a priori* considerations, relating to the experimental conditions. After this procedure the formulae (3) and (4) give the required covariances in addition to the errors of the tabulated quantities.

Let us examine this approach in greater detail by considering two examples: the compilation of calorimetry data alone and of equilibrium data alone.

Compilation of calorimetric data. We shall discuss the simplest system. Assume that all the available input data have been obtained in calorimetric experiments: the vector of the experimental reaction enthalpies $\Delta_r H = (\Delta_r H_1^o, \ldots, \Delta_r H_n^o)'$ (from combustion and dissolution calorimetry) and the vector of the reduced Gibbs free energies $\Phi = \{\Phi_1^o, \ldots, \Phi_m^o\}'$ (from the integrals of the measured specific heat of the individual substances). To simplify the treatment we shall assume that all the reaction enthalpies have been measured at the standard temperature.

In this formulation of the problem the dispersion matrix $\mathcal{D}(\Phi)$ has a diagonal form, since the Φ_i^o values for the different substances have been obtained in independent experiments. The covariance matrix cov$(\Delta_f H, \Phi)$ is also zero, since the enthalpies of formation are obtained only from the reaction enthalpies without a contribution from the reduced Gibbs free energies. Therefore the only remaining problem is the dispersion matrix $\mathcal{D}(\Delta_f H)$, which can contain nondiagonal terms [the covariances between different enthalpies of formation, cov$(\Delta_i H_i^o, \Delta_j H_j^o)$].

We shall assume that all the enthalpies of reaction have been measured in independent experiments. In other words, the dispersion matrix $\mathcal{D}(\Delta_r H)$ has a diagonal form. We shall write it as

$$\mathcal{D}(\Delta_r H) = \sigma^2 \text{diag}(W_1^{-1}, \ldots, W_n^{-1}), \qquad (6)$$

where W_i is the weight of the i-th reaction, and σ^2 is the dispersion for unit weight.

The relationship between the enthalpies of formation and the enthalpies of the reactions will be written

$$\mathcal{V}'\Delta_t H = \Delta_r H, \qquad (7)$$

where $\mathcal{V}$ is the stoichiometric matrix

$$\mathcal{V} = (v_1, \ldots, v_n).$$

The rank of the matrix $\mathcal{V}$ is always less than the number of substances taking part in all the n reactions: rank$(\mathcal{V}) < m$ (as a result of the law of conservation of mass of the elements in chemical reactions). In practice this means that all substances should be divided into two subsets: the subset A, with known enthalpies of formation, and the subset B, with unknown enthalpies of formation. Accordingly, the vector of the enthalpies of formation and the stoichiometric matrix are written

$$\Delta_t H = \left[\begin{array}{c} \Delta_t H_A \\ \Delta_t H_B \end{array} \right] \quad \mathcal{V} = (\mathcal{V}_A, \mathcal{V}_B),$$

and Eqn. (7) becomes

$$\mathcal{V}_B\Delta_t H_B = \Delta_r H - \mathcal{V}_A\Delta_t H_A. \qquad (8$$

In general the classification of substances into two subsets should be based on a definition which makes the enthalpy of formation of simple substance in the standard state identically equal to zero, i.e. in which the subset A contains elements in their standard state and contains all the other substances.

Eqn. (8) can be solved if the matrix $\mathcal{V}_B$ has an integral rank. If not, the enthalpy of formation of all the substances in the subset cannot be found without determining additional experimental reaction enthalpies.

By definition we can write the following equalities for the enthalpy of formation of an element:

$$\Delta_t H_A = 0 \quad \mathcal{D}(\Delta_t H_A) = 0,$$

and use the least squares method with the weighting matrix

$$\mathcal{W} = \mathcal{D}(\Delta_r H)^{-1}.$$

As a result we can express the unknown enthalpies of formation in terms of the experimental reaction enthalpies:

$$\Delta_t H_B = (\mathcal{V}_B'\mathcal{W}\mathcal{V}_B)^{-1}\mathcal{V}_B'\mathcal{W}\Delta_r H.$$

If we now use Eqns. (3) and (6) we obtain an expression for dispersion matrix of the enthalpies of formation:

$$\mathcal{D}(\Delta_t H_B) = \sigma^2(\mathcal{V}_B'\mathcal{W}\mathcal{V}_B)^{-1}.$$

The diagonal elements of this matrix are the dispersions of the enthalpies of formation, and the nondiagonal terms are the covariances between the various enthalpies of formation.

The full dispersion matrix of all the enthalpies of formation $\mathscr{D}(\Delta_f H)$ is written

$$\mathscr{D}(\Delta_f H) = \mathscr{D}\begin{bmatrix} \Delta_t H_B \\ \Delta_t H_A \end{bmatrix} = \begin{bmatrix} \mathscr{D} \dfrac{(\Delta_t H_B)}{0} & 0 \\ 0 & 0 \end{bmatrix}. \qquad (11)$$

The formulae (10) and (11) are the solution of the first problem. However, using this classification (A for the elements in their standard state, B for the other substances) we are often forced to include a very large number of reactions (so as to obtain the full rank of the matrix $\mathscr{V}_B$). For example, if we wish to use this classification to compile handbooks comparable to the existing tabulations[1,2] we need to solve a system of $\sim 10\,000$ equations with ~ 1000 unknowns. It would also not be forgotten that after solving this system of equations once we shall need to solve it a second time when the experimental data for new substances have been added to it.

The successive inclusion of experimental reaction enthalpies involving new substances is a more convenient approach. In the first step the enthalpies of formation of some substances are determined by using formulae (9)—(11). These substances can then be included in the subset A with known enthalpies of formation. This calls for some modification of the equations given above, since $\Delta_f H_A$ and $\mathscr{D}(\Delta_f H_A)$ are now $\neq 0$, though they are known.

The first equation to be answered when solving the system of equations (8) by least squares is: should the dispersion matrix $\mathscr{D}(\Delta_f H_A)$ be included in the weighting matrix $\mathscr{W}$? In order to answer we must examine the conversion of (7) into (8) more closely. The transformation assumes that we do not wish to change the numerical values of the enthalpies of formation of the substances from the subset A by even the slightest amount, i.e. in the solution of the equations (8) all the enthalpies of formation $\Delta_f H_A$ are treated as exactly known, and the weighting matrix should be the same as that used in the solution of the system of equations (9):

$$\mathscr{W} = \mathrm{diag}(W_1, \ldots, W_n).$$

In the opposite case, if we wish to allow the errors in $\mathscr{D}(\Delta_f H_A)$ when calculating the unknown enthalpies of formation we must not object to a small change in the enthalpies of formation $\Delta_f H_A$ during the solution. Under these conditions the least squares method has to be applied not to the system (8) but to the following system of equations:

$$(\mathscr{V}_A, \mathscr{V}_B) \begin{bmatrix} \Delta_t H_A \\ \Delta_t H_B \end{bmatrix} = \Delta_r H,$$

$$\mathscr{E}\Delta_t H_A = \Delta_t H_A, \qquad (12)$$

where $\mathscr{E}$ is the unitary matrix.

The change from (12) to (8) is possible only by ignoring the error $\mathscr{D}(\Delta_f H_A)$ and writing the solution in the form

$$\Delta_t H_B (\mathscr{V}_B'\mathscr{W}\mathscr{V}_B)^{-1}\mathscr{V}_B'\mathscr{W}(\Delta_r H - \mathscr{V}_A\Delta_t H_A). \qquad (13)$$

However, in order to determine the full errors of the enthalpies of formation $\Delta_f H_B$ obtained in this way we must allow for the errors in $\Delta_f H_A$ by applying the formula (3) and (4) to Eqn. (13) and treating

the vectors $\Delta_r H$ and $\Delta_f H_A$ as statistically independent $\{\mathrm{cov}\,\Delta_r H, \Delta_f H) = 0\}$. This gives

$$\mathscr{D}(\Delta_t H_B) = \mathscr{A}\{\mathscr{D}(\Delta_r H) + \mathscr{V}_A\mathscr{D}(\Delta_t H_A)\mathscr{V}_A'\}\mathscr{A}',$$

$$\mathrm{cov}(\Delta_t H_B, \Delta_t H_A) = \mathscr{A}\mathscr{V}_A\mathscr{D}(\Delta_t H_A), \qquad (14)$$

where

$$\mathscr{A} = (\mathscr{V}_B'\mathscr{W}\mathscr{V}_B)^{-1}\mathscr{V}_B'\mathscr{W}.$$

The full dispersion matrix of all the enthalpies of formation $\mathscr{D}(\Delta_f H)$ can now be written

$$\mathscr{D}(\Delta_f H) = \mathscr{D}\begin{bmatrix} \Delta_f H_B \\ \Delta_f H_A \end{bmatrix} = \begin{bmatrix} \mathscr{D}(\Delta_f H_B) & \mathrm{cov}(\Delta_f H_B, \Delta_f H_A) \\ \mathrm{cov}(\Delta_f H_A, \Delta_f H_B) & \mathscr{D}(\Delta_f H_A) \end{bmatrix}, \qquad (15)$$

where the matrix $\mathscr{D}(\Delta_f H_A)$ should be given before the calculation of $\Delta_f H_B$, and the other matrices are calculated by Eqns. (14).

Compilation of equilibrium data. There are two ways of obtaining the enthalpies of reactions from equilibrium constants: in the slang of practical thermodynamics they are called the second-law and the third-law calculation. The first approach uses the temperature dependence of the equilibrium constants, whereas the second uses the absolute values of $\Delta_r S^\circ$ ($\Delta_r \Phi^\circ$) calculated from the absolute entropies of the substances. We shall discuss only the third-law method, because it is most often used in the compilation of equilibrium constants. When the second-law calculation is used it is more difficult to assemble a set of mutually consistent thermodynamic data.[1,2]

Assume that the equilibrium constants $K_{i,j}^\circ$ have been measured for n reactions. The subscript i gives the number of the reaction, $i = 1, \ldots, n$; the subscript j identifies the measured equilibrium constant in the i-th reaction. To determine the unknown enthalpies of formation we must minimise the following sum of squares deviations:

$$\sum_{i,j}\left(R\ln K_{i,j}^\circ + \frac{v_i'\Delta_t H}{T_{i,j}} - v_i'\Phi\right)^2 w_{i,j}, \qquad (16)$$

where $w_{i,j}$ is the weight of the equilibrium constant $K_{i,j}^\circ$. In the third-law calculation the vector Φ is assumed to be known *a priori*. In that case, as we have shown,[4] the minimum in the sum of squared deviations (16) is reached simultaneously with the minimum of

$$\sum_i (\Delta_r H_i^\circ - v_i\Delta_t H)^2 W_i, \qquad (17)$$

where $\Delta_r H_i^\circ$ is the average experimental enthalpy of the i-th reaction,

$$\Delta_r H_i^\circ = \sum_j (v_i\Phi - R\ln K_{i,j}^\circ)w_{i,j}T_{i,j}^{-1} \Big/ \sum_j w_{i,j}T_{i,j}^{-2}, \qquad (18)$$

and W_i is the weight assigned to the i-th reaction,

$$W_i = \sum_j w_{i,j}T_{i,j}^{-2}. \qquad (19)$$

This means that the equilibrium constants can be calculated independently for each reaction, so as to obtain the enthalpies of the reactions. A system of equations entirely analogous to the system (7) is thus obtained whose solution is also given by Eqn. (13).

We note that the errors in the reduced Gibbs free energies Φ are not used in determining the weight of the reaction enthalpies in formula (19). This aspect was discussed above in the section on the errors in $\Delta_f H_A$. When finding the minimum of the sum of squared deviations (16) we do not wish to alter the Φ values used in the calculation even by the smallest amount. This means that in the calculation of the reaction enthalpies (and therefore also of the enthalpies of formation) the Φ values are treated as exact.

However, after finding the enthalpies of formation by Eqn. (13) we must allow for the errors in all the quantities used in the calculation in order to determine their full error. To simplify the treatment the arguments to follow will be developed in the approximation of temperature independence of the reduced Gibbs free energies and of their errors. This will make clear all the main features of the problem and will give a reasonably good first approximation. Without this assumption both the derivations and the final formulae would be extremely elaborate without any gain in information content.

We transform Eqn. (18) treating Φ as constant:

$$\Delta_r H_i^{\circ} = Y_i + T_i \nu_i' \Phi,$$

where Y_i is a function of the experimental equilibrium contants,

$$Y_i = -\sum_j R \ln K_{i,j}^{\circ} w_{i,j} T_{i,j}^{-1} \Big/ \sum_j w_{i,j} T_{i,j}^{-2},$$

and T_i is the mean temperature of the i-th reaction,

$$T_i = \sum_j T_{i,j}^{-1} \Big/ \sum_j T_{i,j}^{-2}.$$

We now re-write the equation in the matrix form

$$\Delta_r H = Y + \mathscr{T}\mathscr{V}\Phi,$$

where $\mathscr{T} = \mathrm{diag}(T_1, \ldots, T_n)$, and we insert this simplified expression into Eqn. (13)

$$\Delta_f H_a = \mathscr{A}(Y + \mathscr{T}\mathscr{V}\Phi - \mathscr{V}_A \Delta_f H_A). \tag{20}$$

Eqn. (20) gives the relationship between the calculated enthalpies of formation and the initial quantities: equilibrium constants, reduced Gibbs free energies, and given enthalpies of formation. Eqns. (3) and (4) can now be used. The only remaining problem is to establish whether non-zero covariances between the three vectors used in the calculation are present.

The vector Y was obtained exclusively from experimental equilibrium constants, without using Φ or $\Delta_f H_A$. This means that the covariance matrices between Y and Φ or between Y and $\Delta_f H_A$ are zero.

However, whether the covariance matrix $\mathrm{cov}(\Delta_f H_a, \Phi)$ is zero depends on how the subset A (consisting of substances with known enthalpies of formation) was assembled. In order to satisfy the condition $\mathrm{cov}(\Delta_f H, \Phi) = 0$ the enthalpies of formation of the substances in the subset A must be determined only from calorimetric experiments, without using the reduced Gibbs free energies, which can always be done by expanding the set of reactions. Unless this is done we have $\mathrm{cov}(\Delta_f H_A) \neq 0$, and the

covariances from this matrix must be given. However, in any we can write

$$\mathscr{D}(\Delta_t H_a) = \mathscr{A}\{\mathscr{D}(Y) + \mathscr{T}\mathscr{V}\mathscr{D}(\Phi)\mathscr{V}'\mathscr{T} + \mathscr{V}_B \mathscr{D}(\Delta_t H_A)\mathscr{V}_A' - \\ -\mathscr{T}\mathscr{V}\,\mathrm{cov}(\Phi,\,\Delta_t H_A)\mathscr{V}_A' - \mathscr{V}_A'\,\mathrm{cov}(\Delta_t H_A,\,\Phi)\mathscr{V}'\mathscr{T}\}\mathscr{A}',$$

$$\mathrm{cov}(\Delta_t H_a,\,\Delta_t H_A) = \mathscr{A}\mathscr{T}\mathscr{V}\,\mathrm{cov}(\Phi,\,\Delta_t H_A) - \mathscr{A}\mathscr{V}_A\mathscr{D}(\Delta_t H_A),$$

$$\mathrm{cov}(\Delta_t H_a,\,\Phi) = \mathscr{A}\mathscr{T}\mathscr{V}\mathscr{D}(\Phi) - \mathscr{A}\mathscr{V}_A\,\mathrm{cov}(\Delta_t H_A,\,\Phi).$$

The full dispersion matrix for all the quantities to be tabulated

$$\mathscr{D}\begin{bmatrix}\Delta_f H_B \\ \Delta_f H_A \\ \Phi\end{bmatrix} = \begin{bmatrix} \mathscr{D}(\Delta_f H_B) & \mathrm{cov}(\Delta_f H_B,\,\Delta_f H_A) & \mathrm{cov}(\Delta_f H_B,\,\Phi) \\ \mathrm{cov}(\Delta_f H_A,\,\Delta_f H_B) & \mathscr{D}(\Delta_f H_A) & \mathrm{cov}(\Delta_f H_A,\,\Phi) \\ \mathrm{cov}(\Phi,\Delta_f H_B) & \mathrm{cov}(\Phi, \Delta H_f H_A) & \mathscr{D}(\Phi) \end{bmatrix}$$

The dispersion matrices $\mathscr{D}(\Delta_f H_A)$ and $\mathscr{D}(\Phi)$ and the covari matrix $\mathrm{cov}(\Delta_f H_A,\,\Phi)\{\mathrm{cov}(\Phi,\,\Delta_f H_A)\mathrm{cov}(\Delta_f H_A,\,\Phi)'\}$ must known before formula (13) is used; the other quantities calculated by Eqns. (21)—(23).

References

1. V P Glushko (Editor) *Termodinamicheskie Svoistva Individual'nykh Veshchestv* (Thermodynamic Properties of Pure Substances), Nauka, Moscow, 1979
2. *JANAF Thermochemical Tables, Second Edition*, Washington D.C., 1971.
3. G A F Seber *Linear Regression Analysis* (Translated into Russian), Mir, Moscow, 1980, 456 pp
4. E B Rudnyi et al. *J. Chem. Thermodyn.*, 1989, **21**(3) 247