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Structural Analysis of Multicomponent Reaction Models:

Part I. Systematic Editing of Kinetic and Thermodynamic Values

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The consistency of a chemical reaction scheme depends in part on the numerical values given for its kinetic and thermodynamic constants. Part 1 of the present two-part treatment provides 1) a systematic procedure to reduce the given values to a self-consistent form, and 2) a proper selection of parameters whenever the values are to be improved by a subsequent regression analysis. Various completeness and consistency tests are described, including a search for illegal reaction loops arising from assumptions of irreversibility. The procedure is implemented on a computer and is illustrated with two examples.

SCOPE

The purpose of this article is to demonstrate a systematic procedure for analyzing a given reaction network and the proposed kinetic and thermodynamic values. This procedure includes consistency tests, which should be performed when several data sources are available, or when any of the reactions are treated as irreversible. It includes completeness tests, to determine whether additional kinetic and thermodynamic values are required. It includes the construction of a consistent set of kinetic and thermodynamic values from the raw data. Finally, there is a selection of adjustable parameters among the kinetic and thermodynamic variables, to allow adjustment of the model to fit additional data from reactor experiments.

It should be noted that the present analysis is not concerned with selecting a reaction network, but rather with testing the consistency of a given network. Nor is any attempt made to combine several inconsistent data in a least-squares sense; that can be done in a subsequent regression. The present procedure selects a subset of the proposed kinetic and thermodynamic values, and compares any redundant values with the solution thus obtained.

CONCLUSIONS AND SIGNIFICANCE

We provide a systematic procedure for editing raw kinetic and thermodynamic coefficients in multicomponent reaction models. The procedure includes several completeness and consistency tests, as well as compact parameterization when the model is to be improved by regression of additional data. The procedure also relieves the engineer of the tedious kinetic and thermodynamic calculations required to bring raw literature values into consistent form. It is particularly useful for large reaction networks, or when values from several sources are to be combined. For example, in the *n*-butane pyrolysis model given by Blakemore and Corcoran (1969), our procedure shows that the initiating reaction (1) should be considered reversible for consistency with the other reactions given.

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Several procedures for systematic computer coding of chemical kinetic schemes have appeared over the last few years (e.g., Silvestri and Zahner 1967, Dickinson and Gelinas 1976). These schemes are designed for simulation of reaction schemes; they do not attempt to analyze the legality of a proposed reaction model nor the consistency of its kinetic and thermodynamic constants. Since the literature demonstrates that errors in problem formulation can occur even with moderately complicated reaction schemes, the present analysis was developed to prevent such mistakes.

PROBLEM STATEMENT

The first steps in reactor simulations are the postulation of a reaction scheme and a literature search for relevant kinetic and thermodynamic values. Here, we assume that these steps have been completed and that a set of relevant kinetic and thermodynamic values is provided in some or all of the following forms.

Kinetic Values (for Non-Equilibrium Reactions)

$k_j(T_j)$	Forward rate constant for reaction j at temperature T_j
$k_j(T_j)/k_l(T_j)$	Ratio of forward rate constants for reactions j and l at temperature T_j
$E_j(T_j)$	Forward activation energy for reaction j, assumed independent of temperature
$E_j(T_j) - E_l(T_j)$	Difference of activation energies for reactions j and l, assumed independent of temperature

Thermodynamic Values

$G_i(T_i)$	Standard Gibbs free energy of species i at temperature T_i
$G_i(T_i) - G_k(T_i)$	Difference of standard free energies of species i and k at temperature T_i
$H_i(T_i)$	Standard enthalpy of species i at temperature T_i
$H_i(T_i) - H_k(T_i)$	Difference of standard enthalpies of species i and k at temperature T_i
$K_j(T_j)$	Equilibrium constant for reaction j at temperature T_j
$K_j(T_j)/K_l(T_j)$	Ratio of equilibrium constants for reactions j and l at temperature T_j
$\Delta H_j(T_j)$	Standard enthalpy change for reaction j at temperature T_j
$\Delta H_j(T_j) - \Delta H_l(T_j)$	Difference of standard reaction enthalpies for reactions j and l at temperature T_j
$\Delta G_j = -\infty$	Irreversibility for reaction j

Here the subscripts i and k are used for species, and j and l are used for reactions. In addition, the molar heat capacity C_{pi} for each species is considered to be given as a function of temperature. Any units consistent with Equations (1)-(4) and (8)-(16) may be used; note that E_j must be in temperature units.

Whenever the simulation is part of a regression of reactor data, the initial kinetic and thermodynamic values in the model must be separated into two groups. The first group should contain those values that are known with sufficient accuracy (known values). The second should contain those values that may be adjusted during a subsequent regression (adjustable parameters). The available values belonging to the latter group are initial estimates. The ratios and differences in the above list of admissible data (k_j/k_l, $E_j - E_l$, etc.) allow use of relative observations, and relative predictions from structure-property correlations. Specifications of this kind allow adjustment of two values such as E_1 and E_2 during a regression while the difference $E_1 - E_2$ remains fixed.

The main task considered here is to convert the available values into a sufficient set of k_j, E_j, G_i, and H_i values, and to select appropriate parameters from among these quantities whenever a regression analysis is to be performed. The selection of G_i and H_i, rather than ΔG_j and ΔH_j, as adjustable parameters ensures consistency of all thermodynamic values. If irreversible reactions are present, some of the G_i and H_i values will not be required, and if equilibrium reactions are present, the corresponding k_j and E_j values will not be required.

FORMULATION OF EQUATIONS FOR KINETIC VALUES

The kinetic quantities k_j and E_j can be determined independently of the thermodynamic quantities. The calculation is straightforward, but is included here for completeness. We start by constructing a set of $2N_r$ linear equations, in which the unknowns are $\ln(k_j)$ and E_j at a prescribed base temperature T_B, and N_r is the number of reactions.

For each available forward rate constant (known or estimated) we have an equation

$$\ln[k_j(T_B)] + (1/T_B - 1/T_j)\, E_j(T_B) = \ln[k_j(T_j)] \tag{1}$$

with a given right-hand term. An Arrhenius frequency factor, for instance, corresponds to a rate constant at $T_j = \infty$. For each available ratio of rate constants, we write

$$\ln[k_j(T_B)] - \ln[k_l(T_B)] + (1/T_B - 1/T_j)\, E_j(T_B) - (1/T_B - 1/T_j)\, E_l(T_B) = \ln[k_j(T_j)/k_l(T_j)] \tag{2}$$

provided that reactions j and l are both regarded as non-equilibrium reactions. These equations include the adjustment of k_j or k_j/k_l from the individual base temperature T_j to the common base temperature T_B.

For each available activation energy, or energy difference, we have an equation

$$E_j(T_B) = E_j(T_j) \tag{3}$$

or

$$E_j(T_B) - E_l(T_B) = E_j(T_j) - E_l(T_j) \tag{4}$$

with E_j treated here as independent of temperature. More detailed temperature dependences could be included by simple changes of the right-hand terms of Equations (1)-(4). In the following development we make the restriction that one equation of type (1) or (2), and one of type (3) or (4), must be provided for each non-equilibrium reaction. The elementary computation of an E_j value from two k_j values at different temperatures is thus omitted here, but is easily done before the main solution.

Equilibrium reactions do not require any forward rate constants or activation energies. For these reactions, we insert dummy values $\ln[k_j(T_B)] = E_j(T_B) = 0$. These values do not propagate in the solution, since Equations (2) and (4) are applied to non-equilibrium reactions only.

SOLUTION OF EQUATIONS FOR KINETIC VALUES

To demonstrate the operations symbolically, we summarize Equations (1)-(4) in the following reordered form:

$$\begin{bmatrix} \mathbf{F}_{11} & \mathbf{F}_{12} \\ \mathbf{F}_{21} & \mathbf{F}_{22} \end{bmatrix} \begin{bmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{bmatrix} = \begin{bmatrix} \mathbf{b}_F \\ \mathbf{b}_E \end{bmatrix} \tag{5}$$

The vector $\mathbf{b}_F$ contains the known right-hand terms, and $\mathbf{b}_E$ those which are designated as initial estimates for a

subsequent regression. The vector $\mathbf{u} = \{\mathbf{u}_1, \mathbf{u}_2\}$ represents the list of unknowns $\ln[k_j(T_B)]$ and $E_j(T_B)$; the distinction between the two parts $\mathbf{u}_1$ and $\mathbf{u}_2$ will develop as the solution proceeds. The matrices $\mathbf{F}_{11}$, $\mathbf{F}_{12}$, $\mathbf{F}_{21}$, and $\mathbf{F}_{22}$ represent the appropriate coefficients in Equations (1)-(4). In actual computations, the reordering is not necessary.

This set of equations is solved by Gauss-Jordan elimination (Hildebrand 1952, Isaacson and Keller 1966). The solution is performed in two stages. During the first, the original columns and rows corresponding to known forward rate data are open for pivot selection; all rows are included in the elimination. When no more pivots can be found the matrix equation will be of the form

$$\begin{bmatrix} \mathbf{I} & \mathbf{F}'_{12} \\ \mathbf{0} & \mathbf{F}'_{22} \end{bmatrix} \begin{bmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{bmatrix} = \begin{bmatrix} \mathbf{b}'_F \\ \mathbf{b}'_E \end{bmatrix} \tag{6}$$

Here $\mathbf{I}$ and $\mathbf{0}$ represent a unit matrix and a null (zero) matrix. This elimination also defines the elements among $\ln(k_j)$ and E_j which belong to the set $\mathbf{u}_1$, namely those whose coefficient columns yielded pivots. The remaining elements belong to $\mathbf{u}_2$.

If any unknowns $\mathbf{u}_2$ are present at this stage, a subsequent regression (not to be treated here) is appropriate to determine them. In preparation for the regression, the matrix solution must be continued. A copy of $\mathbf{b}'_F$ and $\mathbf{F}'_{12}$ is saved, and all k_j and E_j values that appear in $\mathbf{u}_2$ are chosen as adjustable parameters. Then the remaining columns and rows (corresponding to initial estimates) are also opened for pivot selection, and the solution of Equation (6) is continued as far as possible.

The solution will be determinate if and only if each column of the coefficient matrix in Equation (5) yields a pivotal element. Otherwise, we have an incomplete set of input values (i.e., Equation 5 is rank-deficient). It is evident that this will happen if no information is entered into a row of Equation (5). Rank deficiency would also occur if a closed loop of k_j/k_l or $E_j - E_l$ values were specified inadvertently; for example, specifying $E_2 - E_1$, $E_3 - E_2$, and $E_1 - E_3$ is clearly insufficient for the determination of E_1, E_2, and E_3.

If the solution is determinate, it will have the form

$$\begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \end{bmatrix} = \begin{bmatrix} \mathbf{b}''_F \\ \mathbf{b}''_E \end{bmatrix} \tag{7}$$

and we will either have a complete set of known values $\mathbf{u} = \mathbf{u}_1 = \mathbf{b}'_F$ $(= \mathbf{b}''_F)$ in the absence of initial estimates, or a set of initial values $\mathbf{u} = \{\mathbf{u}_1, \mathbf{u}_2\} = \{\mathbf{b}''_F, \mathbf{b}''_E\}$ for a subsequent regression. In the latter case, the solution $\mathbf{u}_1 = \mathbf{b}'_F - \mathbf{F}'_{12}\,\mathbf{u}_2$ saved from Equation (6) is used throughout the regression to relate the dependent quantities $\mathbf{u}_1$ to the adjustable parameters $\mathbf{u}_2$.

FORMULATION OF EQUATIONS FOR THERMODYNAMIC VALUES

The thermodynamic quantities G_i and H_i can be analyzed independently of the kinetic values. This analysis is more complicated than the preceding one, because of the many different ways in which the thermodynamic values can be specified.

We start by constructing a set of linear equations with $2N_c + N_r$ unknowns. Here N_c and N_r are the numbers of chemical species and reactions. The unknowns are taken as G_i, H_i, and $\Delta G_{j,inf}$, at the common base temperature T_B previously introduced. Here $\Delta G_{j,inf}$ is used to represent a large negative ΔG_j value for any reaction that is treated as irreversible.

For each available standard free energy (known or estimated) of a chemical species, we have an equation

$$G_i(T_B) + (T_B/T_i - 1)\,H_i(T_B) = G_i(T_i)\,T_B/T_i + \int_{T_B}^{T_i} T_B/\tilde{T}^2 \int_{T_B}^{\tilde{T}} C_{pi}(T)\,dT\,d\tilde{T} \tag{8}$$

For each available difference of free energies of species, we write

$$G_i(T_B) - G_k(T_B) + (T_B/T_i - 1)\,H_i(T_B) - (T_B/T_i - 1)\,H_k(T_B) = [G_i(T_i) - G_k(T_i)]\,T_B/T_i + \int_{T_B}^{T_i} T_B/\tilde{T}^2 \int_{T_B}^{\tilde{T}} [C_{pi}(T) - C_{pk}(T)]\,dT\,d\tilde{T} \tag{9}$$

Here and below, all values on the right-hand side are given.

For each available enthalpy, or difference of enthalpies of species, we have an equation

$$H_i(T_B) = H_i(T_i) + \int_{T_i}^{T_B} C_{pi}(T)\,dT \tag{10}$$

or

$$H_i(T_B) - H_k(T_B) = H_i(T_i) - H_k(T_i) + \int_{T_i}^{T_B} [C_{pi}(T) - C_{pk}(T)]\,dT \tag{11}$$

These four equations include the adjustment of G_i and H_i from the individual base temperature T_i to the common base temperature T_B.

For each available equilibrium constant (known or estimated) we have an equation

$$\sum_{i=1}^{N_c} \nu_{ji}\,G_i(T_B) + (T_B/T_j - 1) \sum_{i=1}^{N_c} \nu_{ji}\,H_i(T_B) = -RT_B \ln[K_j(T_j)] + \int_{T_B}^{T_j} T_B/\tilde{T}^2 \int_{T_B}^{\tilde{T}} \Delta C_{pj}(T)\,dT\,d\tilde{T} \tag{12}$$

For each available ratio of equilibrium constants, we write

$$\sum_{i=1}^{N_c} (\nu_{ji} - \nu_{li})\,G_i(T_B) + (T_B/T_j - 1) \times \sum_{i=1}^{N_c} (\nu_{ji} - \nu_{li})\,H_i(T_B) = -RT_B \ln[K_j(T_j)/K_l(T_j)] + \int_{T_B}^{T_j} T_B/\tilde{T}^2 \int_{T_B}^{\tilde{T}} [\Delta C_{pj}(T) - \Delta C_{pl}(T)]\,dT\,d\tilde{T} \tag{13}$$

Here the ν_{ji} are the stoichiometric coefficients for reaction j, (i.e. the jth chemical reaction can be written as $\sum_i \nu_{ji} X_i = 0$ where X_i is the ith chemical species). Since all standard-state C_{pi} values are assumed known, we can calculate $\Delta C_{pj} = \sum_i \nu_{ji} C_{pi}$. If a reaction is specified as irreversible, we use the following stoichiometric relation, with a coefficient of unity for the term $-\Delta G_{j,inf}$, and the given value zero on the right-hand side:

$$\sum_{i=1}^{N_c} \nu_{ji}\,G_i(T_B) + (-\Delta G_{j,inf}) = 0 \tag{14}$$

Here $\Delta G_{j,inf}$ represents a large negative value.

For each available reaction enthalpy, or difference of reaction enthalpies, we have an equation

$$\sum_{i=1}^{N_c} \nu_{ji} H_i(T_B) = \Delta H_j(T_j) + \int_{T_j}^{T_B} \Delta C_{pj}(T)\, dT \quad (15)$$

or

$$\sum_{i=1}^{N_c} (\nu_{ji} - \nu_{li}) H_i(T_B) = \Delta H_j(T_j) - \Delta H_l(T_j) + \int_{T_j}^{T_B} [\Delta C_{pj}(T) - \Delta C_{pl}(T)]\, dT \quad (16)$$

These two equations hold whether the reaction is considered reversible or not.

SOLUTION OF EQUATIONS FOR THERMODYNAMIC VALUES

The system of equations just given must now be solved for enough G_i and H_i values, so that all needed ΔG_j and ΔH_j values can be computed. To do this, we solve for as many as possible of the G_i and H_i values in terms of known constants and possibly some unknown G_i and H_i variables. Then we check the latter, to see if they have any net effect on the required ΔG_j and ΔH_j values. Several consistency tests are also performed.

To demonstrate the operations symbolically we summarize Equations (8)-(16) in the following reordered, partitioned form:

$$\begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & 0 \\ S_{21} & S_{22} & S_{23} & S_{24} & 0 \\ S_{31} & S_{32} & S_{33} & S_{34} & 0 \\ S_{41} & S_{42} & S_{43} & S_{44} & 0 \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{bmatrix} = \begin{bmatrix} d_{F1} \\ d_{F2} \\ d_{E1} \\ d_{E2} \\ d_{I1} \\ d_{I2} \end{bmatrix} \quad (17)$$

Here the vector $\mathbf{d}_{F1}$ represents the known right-hand terms that will be selected in the subsequent solution; $\mathbf{d}_{F2}$ represents any known values that prove to be redundant; $\mathbf{d}_{E1}$ and $\mathbf{d}_{E2}$ correspondingly represent the selected and redundant initial estimates; finally, $\mathbf{d}_{I1}$ and $\mathbf{d}_{I2}$ denote the zero right-hand terms arising from selected and redundant specifications of irreversibility. At this initial stage, it is impossible to allocate the elements between $\mathbf{d}_{F1}$ and $\mathbf{d}_{F2}$; between $\mathbf{d}_{E1}$ and $\mathbf{d}_{E2}$; or between $\mathbf{d}_{I1}$ and $\mathbf{d}_{I2}$. That selection will be done by the following Gauss-Jordan elimination. The vector $\mathbf{v} = \{v_1, v_2, v_3, v_4, v_5\}$ represents the unknowns $G_i(T_B)$, $H_i(T_B)$, and $\Delta G_{j,inf}$, as classified below. The vector $\mathbf{v}_1$ represents the pivotal variables G_i and H_i that will be selected in the solution of rows $\mathbf{d}_{F1}$; $\mathbf{v}_2$ represents the pivotal variables selected in the solution of rows $\mathbf{d}_{E1}$; $\mathbf{v}_3$ represents any unknowns that can be assigned arbitrarily (these thermodynamic base values are set equal to zero); $\mathbf{v}_4$ represents the pivotal variables selected in the solution of rows $\mathbf{d}_{I1}$; and $\mathbf{v}_5$ represents a vector of symbolic infinite values $\Delta G_{j,inf}$, usable to denote irreversible reactions. The matrices S_{ij} represent the coefficients in Equations (8)-(16). In actual computations, we do not reorder the rows and columns, but simply label them as the solution proceeds.

The above set of equations is solved by Gauss-Jordan elimination. The solution is performed in four stages. To begin, all columns (variables) not corresponding to initial estimates for species are opened for pivot selection, and all rows with known right-hand terms ($\mathbf{d}_{F1}$, $\mathbf{d}_{F2}$) are opened for pivot selection. During the second stage, all remaining G_i and H_i variables are also opened for pivot selection; the $\mathbf{v}_5$ columns, however, will never be opened. This two-stage calculation ensures that the parameters will be chosen as far as possible among those G_i and H_i variables for which initial estimates were specified. As before, the eliminations are performed on all rows, although the selection of pivots is restricted. When no more pivots can be found, the matrix equation will have the form

$$\begin{bmatrix} I & S'_{12} & S'_{13} & S'_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & S'_{32} & S'_{33} & S'_{34} & 0 \\ 0 & S'_{42} & S'_{43} & S'_{44} & 0 \\ 0 & S'_{52} & S'_{53} & S'_{54} & S'_{55} \\ 0 & S'_{62} & S'_{63} & S'_{64} & S'_{65} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{bmatrix} = \begin{bmatrix} d'_{F1} \\ d'_{F2} \\ d'_{E1} \\ d'_{E2} \\ d'_{I1} \\ d'_{I2} \end{bmatrix} \quad (18)$$

The pivot selection during these first two solution stages defines the elements in $\mathbf{v}_1$ and $\mathbf{d}_{F1}$. We have now solved for $\mathbf{v}_1$ in terms of the unknowns $\mathbf{v}_2$, $\mathbf{v}_3$, and $\mathbf{v}_4$. The coefficients in the rows corresponding to $\mathbf{d}'_{F2}$ are completely reduced to zero. If any non-zero coefficient had been present in a $\mathbf{d}'_{F2}$ equation at this stage, it would have been possible to select that element as pivot and perform one more elimination.

If any unknowns $\mathbf{v}_2$, $\mathbf{v}_3$, and $\mathbf{v}_4$ are present at this stage, a subsequent regression (not treated here) may be appropriate to determine some of them. To prepare for this, the matrix solution must be continued. A copy of $\mathbf{d}'_{F1}$ and S'_{12} is saved. Then during a third stage, all rows with estimated right-hand terms ($\mathbf{d}'_{E1}$, $\mathbf{d}'_{E2}$) are also opened for pivot selection, and the solution is continued. At the end of this stage, the matrix equation has the form

$$\begin{bmatrix} I & 0 & S''_{13} & S''_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & I & S''_{33} & S''_{34} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & S''_{53} & S''_{54} & S''_{55} \\ 0 & 0 & S''_{63} & S''_{64} & S''_{65} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \end{bmatrix} = \begin{bmatrix} d''_{F1} \\ d''_{F2} \\ d''_{E1} \\ d''_{E2} \\ d''_{I1} \\ d''_{I2} \end{bmatrix} \quad (19)$$

The pivot selection during this third stage defines the elements in $\mathbf{v}_2$ and $\mathbf{d}_{E1}$. We shall see later that the variables selected for $\mathbf{v}_2$, although based on initial estimates, may not all be required as adjustable parameters. We have now solved for $\mathbf{v}_1$ and $\mathbf{v}_2$ in terms of the remaining unknowns $\mathbf{v}_3$ and $\mathbf{v}_4$, and the coefficients in the rows corresponding to $\mathbf{d}''_{E2}$ have been reduced to zero.

We are now ready to test the completeness and consistency of the finite thermodynamic values. To test for completeness, we consider the columns corresponding to $\mathbf{v}_3$ and $\mathbf{v}_4$, from which no pivots have been selected, and see whether these missing G_i and H_i values are needed. From Equation (19), we obtain the other thermodynamic variables, $\mathbf{v}_1$ and $\mathbf{v}_2$, in terms of $\mathbf{v}_3$ and $\mathbf{v}_4$

$$\mathbf{v}_1 = \mathbf{d}''_{F1} - S''_{13}\mathbf{v}_3 - S''_{14}\mathbf{v}_4 \quad (20)$$

$$\mathbf{v}_2 = \mathbf{d}''_{E1} - S''_{33}\mathbf{v}_3 - S''_{34}\mathbf{v}_4 \quad (21)$$

Through use of the stoichiometric matrix ν we formally recompute ΔG_j and ΔH_j for all reversible reactions. If the reaction model is to be used for non-isothermal reactors, we also recompute all remaining ΔH_j. Any dependence of a finite ΔG_j or ΔH_j on a $\mathbf{v}_3$ or $\mathbf{v}_4$ unknown indicates incomplete data. Calculation continues only if there is no such dependence, i.e., if $\mathbf{v}_3$ and $\mathbf{v}_4$ are either empty

or redundant. Redundancy can arise from irreversibility specifications, or from the arbitrariness of certain thermodynamic base values.

To test the finite thermodynamic values for consistency, we consider the rows corresponding to $\mathbf{d}''_{F2}$ and $\mathbf{d}''_{E2}$. The coefficients in these rows have been reduced to zero, and each right-hand element is a measure of inconsistency among the finite thermodynamic values.

This completes the treatment of the finite data, and we can make an initial consistency test of the postulated irreversible reactions. If any row of $\mathbf{S}''_{53}$ and $\mathbf{S}''_{54}$, or of $\mathbf{S}''_{63}$ and $\mathbf{S}''_{64}$, is completely reduced to zero, we have a reaction specified as irreversible, but for which other data give a finite ΔG_j. If this occurs, the model should be revised.

A fourth solution stage is performed, during which all rows corresponding to irreversible reactions ($\mathbf{d}''_{I1}$, $\mathbf{d}''_{I2}$) are also opened. Recall that the $\mathbf{v}_5$ columns are still closed. This step prepares for another consistency test of the irreversibility specifications. At the end of this stage, the matrix equation takes the form

$$\begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{S}'''_{13} & \mathbf{0} & \mathbf{S}'''_{15} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} & \mathbf{S}'''_{33} & \mathbf{0} & \mathbf{S}'''_{35} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{S}'''_{53} & \mathbf{I} & \mathbf{S}'''_{55} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{S}'''_{65} \end{bmatrix} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \\ \mathbf{v}_3 \\ \mathbf{v}_4 \\ \mathbf{v}_5 \end{bmatrix} = \begin{bmatrix} \mathbf{d}'''_{F1} \\ \mathbf{d}'''_{F2} \\ \mathbf{d}'''_{E1} \\ \mathbf{d}'''_{E2} \\ \mathbf{d}'''_{I1} \\ \mathbf{d}'''_{I2} \end{bmatrix} \tag{22}$$

The pivot selection during this fourth stage defines the elements in $\mathbf{v}_4$ and $\mathbf{d}_{I1}$. The $\mathbf{v}_4$ variables will all be redundant according to the completeness test described above.

To examine the consistency of the irreversible reactions, we consider the rows of $\mathbf{S}'''_{65}$, from which no pivots have been selected. Each of these gives a linear combination of $\Delta G_{j,inf}$ values which must equal the finite right-hand term given in $\mathbf{d}'''_{I2}$. Such an equation represents a reaction string for which the overall ΔG is finite. The string contains one or more irreversible reactions (identified by the non-zero elements of the row) and may contain reversible steps as well. A special case of such a string is a closed loop of irreversible reactions, for which the net ΔG of course is zero. However, the string (or loop) is legal if the row contains at least one negative element. The diagonal elements of $\mathbf{S}'''_{65}$ are unity; hence, any off-diagonal negative element ensures that the net ΔG for the string contains $\Delta G_{j,inf}$ terms of both signs, and thus can be finite, in agreement with the right-hand term.

To complete the test, we examine the legality of all linear combinations of the rows (or reaction strings) in $\mathbf{S}'''_{65}$. These rows contain a unit matrix (the coefficients of the variables $\mathbf{v}_5$; see Equation 14). Hence, any difference of rows contains $+1$ and -1 as elements and is legal, by the sign rule of the preceding paragraph. Therefore, we need only examine sums of rows. The legality of all possible combinations of rows can be investigated in the following way: Search for a column of $\mathbf{S}'''_{65}$ with no element greater than zero. Then find each negative element of that column, and remove the corresponding row (reaction string) of $\mathbf{S}'''_{65}$. It is obvious that no matter how such a row is added to any other, it will produce a negative element in that column and, hence, a legal string.

Then search for another such column of the reduced $\mathbf{S}'''_{65}$ and remove additional rows in the same manner. If all rows of $\mathbf{S}'''_{65}$ can be thus removed, the assumptions of irreversibility are self-consistent. Otherwise, the original reaction scheme contains either a closed loop with one or more irreversible reactions, all going in the same direction, or a sum of irreversible reactions, for which the other data indicate a finite total ΔG. In either case, the reaction scheme must be revised.

This completes the formal tests of the reaction scheme, and the evaluation or initial estimation of the needed thermodynamic properties.

SELECTION OF PARAMETERS AMONG THE THERMODYNAMIC VALUES

If a subsequent regression is to be performed, we have to select a basis of adjustable parameters, $\mathbf{v}_{2a}$, among the variables $\mathbf{v}_2$. Let $\mathbf{v}_{2b}$ be those elements of $\mathbf{v}_2$ that are not included in $\mathbf{v}_{2a}$, and set $\mathbf{v}_3$ and $\mathbf{v}_4$ equal to zero. The values in $\mathbf{v}_{2b}$, although based on initial estimates, will be thermodynamic base values and can be maintained fixed during the regression. We now construct the matrix equation

$$\begin{bmatrix} \mathbf{I} & \mathbf{S}'_{12a} & \mathbf{S}'_{12b} \\ \boldsymbol{\nu}_{21} & \boldsymbol{\nu}_{22a} & \boldsymbol{\nu}_{22b} \\ \boldsymbol{\nu}_{31} & \boldsymbol{\nu}_{32a} & \boldsymbol{\nu}_{32b} \end{bmatrix} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{v}_{2a} \\ \mathbf{v}_{2b} \end{bmatrix} = \begin{bmatrix} \mathbf{d}'_{F1} \\ \mathbf{f}_{E2} \\ \mathbf{f}_{E3} \end{bmatrix} \tag{23}$$

in which the first set of equations is taken directly from the first line of Equation (18). The last two sets together represent the stoichiometric relations for all finite ΔG_j and ΔH_j (the right-hand elements) in terms of the non-zero G_i and H_i values. The distinction between the latter two sets of equations will appear when the solution is obtained.

Equation (23) is solved in two stages. First $\mathbf{v}_1$ is eliminated from the second and third sets of equations, and then the latter are solved as far as possible. This gives the desired identification of the parametric variables $\mathbf{v}_{2a}$:

$$\begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{S}''_{12b} \\ \mathbf{0} & \mathbf{I} & \boldsymbol{\nu}'_{22b} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{v}_{2a} \\ \mathbf{v}_{2b} \end{bmatrix} = \begin{bmatrix} \mathbf{f}'_F \\ \mathbf{f}'_{E2} \\ \mathbf{f}'_{E3} \end{bmatrix} \tag{24}$$

These equations indicate directly that the variables represented by $\mathbf{v}_{2a}$ form a basis of all the parameters. The variables represented by $\mathbf{v}_{2b}$ can be maintained as fixed base values during the regression. The initial values for $\mathbf{v}_{2a}$ and $\mathbf{v}_{2b}$ are given by $\mathbf{d}''_{E1}$ as shown in Equation (21). This implies that we have no need for the right-hand sides in Equations (23) and (24).

EXAMPLE 1

This example demonstrates 1) the presence and handling of inconsistent initial estimates; 2) the combining of known values with initial estimates; and 3) the assignment of constants, base values and parameters when initial estimates for regression are provided.

Consider the following reaction scheme with four components and four reactions, and the indicated set of estimated and known thermodynamic values, all given at the desired common base temperature:

$$P_1 \overset{a}{\rightleftharpoons} P_2 \qquad G_1 = 10 \text{ (est)} \qquad \Delta H_a = 100 \text{ (est)}$$

$$P_2 \overset{b}{\rightleftharpoons} P_3 \qquad G_2 = 20 \text{ (est)} \qquad \Delta H_b = 200 \text{ (est)}$$

$$P_3 \overset{c}{\rightleftharpoons} P_4 \quad G_3 = 30 \text{ (est)} \quad \Delta H_c = 300$$

$$P_4 \overset{d}{\rightleftharpoons} P_1 \quad G_4 = 40 \text{ (est)} \quad \Delta H_d = 400 \text{ (est)}$$

$$\Delta G_c = 5$$

To analyze this set of thermodynamic values we set up Equation (17):

	G1	G2	G3	G4	H1	H2	H3	H4		
G1	1									10
G2		1								20
G3			1							30
G4				1						40
ΔGc			−1	1					=	5
ΔHa					−1	1				100
ΔHb						−1	1			200
ΔHc							−1	1		300
ΔHd					1			−1		400

No columns are opened for pivot selection during the first transformation stage. During the second stage, all columns are opened and rows {5, 8} are opened. This allows two transformations, giving

	G1	G2	G3*	G4	H1	H2	H3*	H4		
G1	1									10
G2		1								20
G3				1						35
G4				1						40
ΔGc*			1	−1					=	−5
ΔHa					−1	1				100
ΔHb						−1		1		500
ΔHc*							1	−1		−300
ΔHd					1			−1		400

Here the * indicates that a pivot was selected from the corresponding column or row. During the third stage all remaining rows are also opened for pivot selection. This allows five additional transformations, giving the following result in the form of Equation (19):

	G1*	G2*	G3*	G4*	H1*	H2*	H3*	H4		
G1*	1									10
G2*		1								20
G3*			1							35
G4										5
ΔGc*				1					=	30
ΔHa*					1			−1		−600
ΔHb*						1		−1		−500
ΔHc*							1	−1		−300
ΔHd										1000

The completeness test requires examination of H_4 (column 8) only. No pivot was selected in this column, and according to the solution just given we have

$$H_1 = H_4 - 600$$

$$H_2 = H_4 - 500$$

$$H_3 = H_4 - 300$$

in agreement with Equations (20) and (21). A simple recalculation of all ΔH values with these expressions shows that the value of H_4 is redundant and may be set arbitrarily to zero.

The consistency test requires examination of rows 4 and 9. No pivots were selected in these rows; hence the original right-hand values, 40 and 400, are redundant. The present right-hand terms, 5 and 1000, are the deviations of the original right-hand terms from consistency with the chosen solution. The reaction scheme does not contain any irreversible reactions; therefore, a fourth transformation is not needed.

The matrix obtained after the third transformation stage indicates that G_1, G_2, G_4, H_1, and H_2 may possibly be treated as parameters. To examine how many of these should be parameters we set up the coefficient matrix of Equation (23):

	G1	G2	G3*	G4	H1	H2	H3*
ΔGc*			1	−1			
ΔHc*							1
ΔGa	−1	1					
ΔGb		−1	1				
ΔGc			−1	1			
ΔGd	1			−1			
ΔHa					−1	1	
ΔHb						−1	1
ΔHc							−1
ΔHd					1		

This matrix is transformed in two stages. During the first stage, we open columns {3, 7} and rows {1, 2} for pivot selection and perform two eliminations. During the second stage, we open all remaining columns and rows. This allows G_1, G_2, H_1, and H_2 to be selected as pivots; rank deficiency prevents selection of G_4. The current estimate for G_4 may be used as a base value, but should not be selected as a parameter in a regression analysis.

With these modifications, the standard-state thermodynamic values at T_B become

$$G_1 = 10 \text{ (par)} \qquad H_1 = -600 \text{ (par)}$$
$$G_2 = 20 \text{ (par)} \qquad H_2 = -500 \text{ (par)}$$
$$G_3 = 30 \qquad H_3 = -300$$
$$G_4 = 35 \qquad H_4 = 0$$

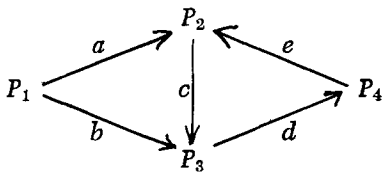
giving four parameters and four fixed values; the original values

$$G_4 = 40 \qquad \Delta H_d = 400$$

are omitted.

EXAMPLE 2

This example demonstrates how assumptions of irreversibility may give rise to illegal reaction loops. Consider the following reaction scheme with four species and five irreversible reactions:



To examine this scheme, we set up Equation (17) as usual. The free-energy equations contain only the following non-zero coefficients:

	G1	G2	G3	G4	Ia	Ib	Ic	Id	Ie
ΔGa	−1	1			1				
ΔGb	−1		1			1			
ΔGc		−1	1				1		
ΔGd			−1	1				1	
ΔGe		1		−1					1

No rows are opened for pivot selection during the first three transformation stages. During the fourth, we open columns {1, 2, 3, 4} and all rows for pivot selection. This allows three transformations, giving

	G1*	G2*	G3*	G4	Ia	Ib	Ic	Id	Ie
ΔGa*	1			−1		−1		−1	
ΔGb*		1		−1	1	−1		−1	
ΔGc					1	−1	1		
ΔGd*			1	−1				−1	
ΔGe					−1	1		1	1

Here no pivots were selected from rows 3 and 5. These rows constitute two linearly independent closed loops $\{a, -b, c\}$ and $\{-a, b, d, e\}$, both of which happen to be legal. However, in order to consider all other possibilities, we extract these rows from the transformed unit matrix

	Ia	Ib	Ic	Id	Ie
ΔGc	1	−1	1		
ΔGe	−1	1		1	1

Since we cannot find a column without positive elements, the reaction scheme must contain an illegal string of irreversible reactions. For instance, an illegal loop $\{c, d, e\}$ can be obtained by addition of the two strings found above. The rest of the array in Equation (17) transforms in the usual way, but has been omitted here for brevity.

This example corresponds to an isomerization system. It was chosen for ease of visualization, and is, in fact, solvable by inspection of its planar graph. More complicated reaction networks are difficult to study graphically, but are readily tested by the method given here.

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Part II. Formulation of Mass Balances and Thermodynamic Constraints

Simulation of chemical reactors requires the formulation of mass balances, often coupled with thermodynamic constraints such as ionization and chemisorption equilibria. We provide a systematic procedure for selecting the smallest sufficient set of dependent variables and a corresponding set of mass balances. The procedure depends on the type of reactor, and is developed for two common reactor types. The procedure is implemented on a computer and illustrated by examples from catalysis and electrochemistry.

SCOPE

Several steps are required preparatory to simulating a chemical reactor. In Part I, we considered the analysis of the proposed kinetic and thermodynamic values for the reaction scheme. Here we formulate a set of transport equations (mass and energy balances) and a corresponding set of dependent variables (concentrations, temperature,

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