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

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

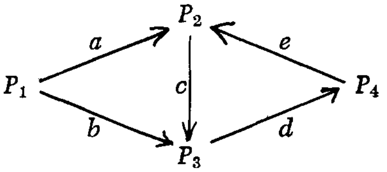
giving four parameters and four fixed values; the original values

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

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:

$$\begin{array}{c|cccc|ccccc|} & G1 & G2 & G3 & G4 & Ia & Ib & Ic & Id & Ie \\ \hline \Delta Ga & -1 & 1 & & & 1 & & & & \\ \Delta Gb & -1 & & 1 & & & 1 & & & \\ \Delta Gc & & -1 & 1 & & & & 1 & & \\ \Delta Gd & & & -1 & 1 & & & & 1 & \\ \Delta Ge & & 1 & & -1 & & & & & 1 \\ \hline \end{array}$$

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

$$\begin{array}{c|cccc|ccccc|} & G1^{*} & G2^{*} & G3^{*} & G4 & Ia & Ib & Ic & Id & Ie \\ \hline \Delta Ga^{*} & 1 & & & -1 & & -1 & & -1 & \\ \Delta Gb^{*} & & 1 & & -1 & 1 & -1 & & -1 & \\ \Delta Gc & & & & & 1 & -1 & 1 & & \\ \Delta Gd^{*} & & & 1 & -1 & & & & -1 & \\ \Delta Ge & & & & & -1 & 1 & & 1 & 1 \\ \hline \end{array}$$

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

$$\begin{array}{c|ccccc|} & Ia & Ib & Ic & Id & Ie \\ \hline \Delta Gc & 1 & -1 & 1 & & \\ \Delta Ge & -1 & 1 & & 1 & 1 \\ \hline \end{array}$$

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.

ACKNOWLEDGMENT

This work was supported by Grant ENG 76-24368 from the National Science Foundation, and by the University of Wisconsin-Madison Graduate School Research Committee.

LITERATURE CITED

Blakemore, J. E. and W. H. Corcoran, "Validity of the Steady-State Approximation Applied to the Pyrolysis of *n*-Butane," *Ind. Eng. Chem. Proc. Des. Dev.*, 8, 206 (1969).

Dickinson, R. P., Jr., and R. J. Gelinas, "SETKIN: A Chemical Kinetics Preprocessor Code," in *Numerical Methods for Differential Systems*, Academic Press, New York (1976).

Hildebrand, F. B., *Methods of Applied Mathematics*, Prentice Hall, Englewood Cliffs, N.J. (1952).

Isaacson, E., and H. B. Keller, *Analysis of Numerical Methods*, Wiley, New York (1966).

Silvestri, A. J. and J. C. Zahner, "Algebraic Manipulations of the Rate Equations of Certain Catalytic Reactions with a Digital Computer," *Chem. Eng. Sci.*, 22, 465 (1967).

Manuscript received October 14, 1977; revision received June 28, and accepted July 9, 1979.

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,

---

and electrical potential for ionic systems). It is the purpose of this article to provide a systematic procedure for carrying out this formulation.

The procedure includes two types of species (mobile and immobile) and two types of reactions (non-equilibrium and equilibrium). The procedure is developed here for two reactor types. Type I includes the steady one-dimensional plug-flow reactor, the steady well-mixed flow reactor, and the transient well-mixed batch reactor (Guertin et al. 1977, Stewart and Sørensen 1976). Type II includes various steady diffusion-reaction systems, such as porous catalytic particles and reactive liquid films, which we will treat further in forthcoming papers.

The present analysis is not concerned with the *solution* of the reactor equations; only with their consistent formulation. The formulation of appropriate mass balances for reactors may in many cases be fairly simple. But when equilibrium reactions are included, determinate formulations are harder to achieve, and the need for a general procedure becomes apparent.

CONCLUSIONS AND SIGNIFICANCE

Presented here is a systematic method for constructing multicomponent mass balance equations and thermodynamic constraints for chemical reactor simulations. The procedure is based on the specified reaction stoichiometry, *and on simple classifications of the species and reactions.* No specification of elemental compositions of the species is used; isomers and labelled species do not require any special treatment.

Several investigators have analyzed the stoichiometry of chemical reactions in order to simplify chemical reactor simulations (Aris and Mah 1963, Aris 1969, Beek 1962, Prater et al. 1967, Schneider and Reklaitis 1975, Schubert and Hofmann 1976, Schultz et al. 1974). Some of these analyses are based on the elemental compositions of the chemical species and do not invoke a reaction scheme; isomers then give rise to particular difficulties (Whitwell and Dartt 1973). Further difficulties arise in the presence of equilibrium reactions, which yield constraints rather than explicit rate expressions.

PROBLEM STATEMENT

We consider two types of species: mobile and immobile. For steady-state reactors, a species is called "mobile" if its mass balance for a stationary volume element must include outflow (by convection, diffusion, or both). Correspondingly, a species is called "immobile" if its net outflow from a stationary volume element (by convection and diffusion) either vanishes identically or may be neglected. For example, the surface species in a fixed-bed reactor will be treated as immobile, in the sense of being fixed in space. Free-radical intermediate species in a flowing fluid are sometimes treated as immobile, in that their net outflow from a volume element is negligible compared with their rates of formation and consumption; this is the well-known "pseudo-steady-state approximation" of chemical kinetics.

For transient reactors, the mobile species are correspondingly defined as those whose mass balances must include an accumulation, convection or diffusion term. The rest of the species are called immobile. Here, as in steady flow reactors, immobility may be invoked by use of the pseudo-steady-state approximation for free-radical intermediate species. Surface concentrations, on the other hand, will now be time-dependent; hence these species should be considered mobile unless one invokes the pseudo-steady-state approximation for them. In view of this, the conventional analogy between the steady plug-flow reactor and the transient well-stirred batch reactor requires either 1) the absence of surface species, or 2) pseudo-steady-state assumptions for the surface species in the transient case. A phase is called mobile if any of its species are; otherwise, it is called immobile.

Reactions are classified as non-equilibrium or equilibrium steps. To describe the non-equilibrium reactions, we need kinetic information (forward rate constants and activation energies) as well as thermodynamic information (equilibrium constants and reaction enthalpies). To describe the equilibrium reactions we will only require thermodynamic information, and regard the forward rate constants as infinite. Each reaction may include both mobile and immobile species.

For the Type I reactor, it is possible to select a basic subset of species, whose concentrations just suffice to determine the concentrations of all species at the corresponding point in the system. The linear relationships needed for this calculation are obtained from the stoichiometric matrix.

For the Type II reactor, on the other hand, we must include all mobile species in the basis, though a basic subset will still suffice for the immobile species. If ionic mobile species are present, we can omit one of those from the basis, and obtain that concentration from the electro-neutrality condition.

In this article, we will first consider the selection of a basic set of species (or smallest sufficient set of dependent variables), and then the construction of a corresponding set of mass balance equations and thermodynamic constraints. Since we have two kinds of species and two kinds of reactions, we select four types of basic concentrations as the dependent variables for the interior part of a mobile phase:

A: mobile species selected from non-equilibrium reactions
B: mobile species selected from equilibrium reactions
C: immobile species selected from non-equilibrium reactions
D: immobile species selected from equilibrium reactions

The remaining species are denoted as non-basic species. The terms "basic" and "non-basic" as used here refer to the status of variables in the Gauss-Jordan elimination.

SELECTION OF BASIC SPECIES FOR TYPE I REACTORS

The selection of a basis (smallest sufficient set) of dependent variables is performed through row operations on the stoichiometric matrix $\boldsymbol{\nu}$. This matrix is defined by

$$\sum_{j} \nu_{ij} \mathcal{R}_j = R_i \qquad (25a)$$

or

$$\boldsymbol{\nu}^T \boldsymbol{\mathcal{R}} = \mathbf{R} \qquad (25b)$$

Here $\boldsymbol{\mathcal{R}}$ is the column vector of reaction rates, and $\mathbf{R}$ is the column vector of production rates of all chemical species. To demonstrate the operations symbolically we write Equation (25b) in the following transposed and reordered form

$$\begin{bmatrix} \mathcal{R}_A \\ \mathcal{R}_B \\ \mathcal{R}_C \\ \mathcal{R}_D \\ \mathcal{R}_{RR} \\ \mathcal{R}_{RN} \end{bmatrix}^T \begin{bmatrix} \nu_{11} & \nu_{12} & \nu_{13} & \nu_{14} & \nu_{15} & \nu_{16} \\ \nu_{21} & \nu_{22} & \nu_{23} & \nu_{24} & \nu_{25} & \nu_{26} \\ \nu_{31} & \nu_{32} & \nu_{33} & \nu_{34} & \nu_{35} & \nu_{36} \\ \nu_{41} & \nu_{42} & \nu_{43} & \nu_{44} & \nu_{45} & \nu_{46} \\ \nu_{51} & \nu_{52} & \nu_{53} & \nu_{54} & \nu_{55} & \nu_{56} \\ \nu_{61} & \nu_{62} & \nu_{63} & \nu_{64} & \nu_{65} & \nu_{66} \end{bmatrix} = \begin{bmatrix} R_A \\ R_B \\ R_C \\ R_D \\ R_{RM} \\ R_{RI} \end{bmatrix}^T \qquad (26)$$

These equations will be solved to express the full vector $\mathbf{R}$ in terms of a basic set of production rates $\{R_A, R_B, R_C, R_D\}$ and a transformed stoichiometric matrix.

The vectors R_A and R_B represent the production rates of the basic "mobile" species that will be selected from the non-equilibrium and equilibrium reactions, respectively. R_C and R_D represent the same for the basic "immobile" species. R_{RM} and R_{RI} represent the production rates of the remaining mobile and immobile species. At this initial stage, it is impossible to distinguish between the elements in the mobile set $\{R_A, R_B, R_{RM}\}$ or between those in the immobile set $\{R_C, R_D, R_{RI}\}$; those distinctions will be made through the choice of pivots in the subsequent Gauss-Jordan elimination.

The first and third rows in Equation (26), associated with $\mathcal{R}_A$ and $\mathcal{R}_C$, represent the non-equilibrium reactions that will be selected in the solution and from which the basic "*A*" and "*C*" species will be chosen. The second and fourth rows, associated with $\mathcal{R}_B$ and $\mathcal{R}_D$, represent the equilibrium reactions that will be selected in the solution and from which basic "*B*" and "*D*" species will be chosen. The last two rows represent any reactions which become stoichiometrically redundant in the transformation.

At this stage it is also impossible to distinguish between the reaction-rate elements in the set $\{\mathcal{R}_A, \mathcal{R}_C, \mathcal{R}_{RR}, \mathcal{R}_{RN}\}$, or between the elements in $\{\mathcal{R}_B, \mathcal{R}_D, \mathcal{R}_{RR}\}$. The two sets may overlap, since the vector $\mathcal{R}_{RR}$ may include both non-equilibrium and equilibrium reactions. The classification shown in Equation (26) will develop as the solution proceeds; hence the reordering of the equations is not possible at this stage.

The solution is obtained by the Gauss-Jordan method (Hildebrand 1952, Isaacson and Keller 1966). The matrix $\boldsymbol{\nu}$ is transformed by linear combination of its rows until no additional pivots can be found. The overall transformation is equivalent to pre-multiplication of $\boldsymbol{\nu}$ by a nonsingular matrix $\mathbf{B}$, and corresponding replacement of $\boldsymbol{\mathcal{R}}^T$ by a new set of reaction rates $\boldsymbol{\mathcal{R}}^T \mathbf{B}^{-1}$. The solution is done in four stages, as described below. Priority is given to equilibrium reactions and immobile species in the elimination, to ensure that a full set of constraints (local equations) will be obtained directly.

During the first stage, all columns corresponding to immobile species (R_C, R_D, R_{RI}), and all rows corresponding to equilibrium reactions ($\mathcal{R}_B$, $\mathcal{R}_D$, part of $\mathcal{R}_{RR}$) are opened for pivot selection; all rows are included in the elimination. The reaction scheme may contain several independent kinds of active surface sites; this does not pose any problem, and all immobile species are allowed as candidates. The species selected here are denoted as basic "*D*" species. When no more pivots can be found, then the remaining equilibrium equations are free of immobile species [i.e., ν'_{23}, ν'_{26}, ν'_{53}, and ν'_{56} have vanished in Equation (27)].

The second stage is then initiated by also opening the columns corresponding to mobile species for pivot selection. The species selected here are denoted as basic "*B*" species. On completion of the second stage, the remaining equilibrium equations are free of all species, and the matrix equation takes the form

$$\begin{bmatrix} \mathcal{R}'_A \\ \mathcal{R}'_B \\ \mathcal{R}'_C \\ \mathcal{R}'_D \\ \mathcal{R}'_{RR} \\ \mathcal{R}'_{RN} \end{bmatrix}^T \begin{bmatrix} \nu'_{11} & 0 & \nu'_{13} & 0 & \nu'_{15} & \nu'_{16} \\ \nu'_{21} & I & 0 & 0 & \nu'_{25} & 0 \\ \nu'_{31} & 0 & \nu'_{33} & 0 & \nu'_{35} & \nu'_{36} \\ \nu'_{41} & 0 & \nu'_{43} & I & \nu'_{45} & \nu'_{46} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \nu'_{61} & 0 & \nu'_{63} & 0 & \nu'_{65} & \nu'_{66} \end{bmatrix} = \begin{bmatrix} R_A \\ R_B \\ R_C \\ R_D \\ R_{RM} \\ R_{RI} \end{bmatrix}^T \qquad (27)$$

At this stage it may also happen that some non-equilibrium reactions have become free of all species. The reactions (equilibrium and non-equilibrium) that are free of all species are represented by $\mathcal{R}_{RR}$, and the corresponding original reactions are linear combinations of the equilibrium reactions that were selected. These reactions are redundant and are discarded.

During the third solution stage, only the columns corresponding to immobile species not yet selected as pivots (R_C, R_{RI}), and the rows corresponding to non-equilibrium reactions, ($\mathcal{R}_A$, $\mathcal{R}_C$, $\mathcal{R}_{RN}$), are opened for pivot selection. The species selected in this stage are denoted as basic "*C*" species. At the end of this stage, ν''_{13}, ν''_{16}, ν''_{63}, and ν''_{66} vanish in Equation (28).

Finally, during the fourth stage, all columns corresponding to mobile species not yet selected as pivots are opened. The species selected here are denoted as basic "*A*" species. At this point, it may happen that some additional rows have vanished and therefore have not been included. This means that certain non-equilibrium reactions (represented by $\mathcal{R}''_{RN}$) are linear combinations of the selected reactions and thus give no further restrictions on the production rates. However, these reactions are still necessary to represent the kinetic scheme. The stoichiometry now takes the form

$$\begin{bmatrix} \mathcal{R}''_A \\ \mathcal{R}''_B \\ \mathcal{R}''_C \\ \mathcal{R}''_D \\ \mathcal{R}''_{RR} \\ \mathcal{R}''_{RN} \end{bmatrix}^T \begin{bmatrix} I & 0 & 0 & 0 & \nu''_{15} & 0 \\ 0 & I & 0 & 0 & \nu''_{25} & 0 \\ 0 & 0 & I & 0 & \nu''_{35} & \nu''_{36} \\ 0 & 0 & 0 & I & \nu''_{45} & \nu''_{46} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} R_A \\ R_B \\ R_C \\ R_D \\ R_{RM} \\ R_{RI} \end{bmatrix}^T \qquad (28)$$

which yields the identities $\mathcal{R}_A'' = R_A$, $\mathcal{R}_B'' = R_B$, $\mathcal{R}_C'' = R_C$, and $\mathcal{R}_D'' = R_D$. Making these substitutions in Equation (28) we obtain the stoichiometric relations for the non-basic species

$$R^T_{RI} = R^T_C \nu''_{36} + R^T_D \nu''_{46} \qquad (29)$$

$$R^T_{RM} = R^T_A \nu''_{15} + R^T_B \nu''_{25} \qquad (30)$$

In the latter equation, we have also applied the steady-state (or the pseudo-steady-state) condition $R_i = 0$ to each immobile species. For the transient well-mixed batch reactor, Equation (30) leads to pseudo-steady-state kinetics; the complete solution may be obtained only by including all species in the mobile set.

Equation (29) may be integrated in time from the original surface state to give the vector of concentration changes (extents) for the immobile species referred to their original states:

$$\boldsymbol{\xi}^T_{RI} = \boldsymbol{\xi}^T_C \, \boldsymbol{\nu}''_{36} + \boldsymbol{\xi}^T_D \, \boldsymbol{\nu}''_{46} \tag{31}$$

Correspondingly, Equation (30) may be integrated along the reactor coordinate (position or time) to give the vector of extents for the mobile species referred to their starting concentrations:

$$\boldsymbol{\xi}^T_{RM} = \boldsymbol{\xi}^T_A \, \boldsymbol{\nu}''_{15} + \boldsymbol{\xi}^T_B \, \boldsymbol{\nu}''_{25} \tag{32}$$

Equations (31) and (32) are the desired linear expressions for the extents of non-basic species in terms of basic species. Ionic species do not require any special treatment.

This completes the selection of basic species for Type I reactors. The construction of the local and spatial reactor equations corresponding to this set of variables will be presented later on.

SELECTION OF BASIC SPECIES FOR TYPE II REACTORS

In the presence of diffusion, the relations among the fluid concentrations are affected by the mass exchange between different fluid elements. Hence, the stoichiometric reduction of the concentration variables for the mobile species can no longer be performed, even though the production rates can be expressed compactly, as before. We can still perform the selection of the basic "*B*," "*C*," and "*D*" species as described above for the Type I reactor, but must include all remaining mobile species as basic "*A*" species. Since all mobile species are included in the basis, there is no need for Equations (30) and (32), and the transformation could be terminated once the "*B*," "*C*," and "*D*" species have been selected. However, in the simulation of diffusion reactors, it is convenient to know the number of independent fluxes. For this reason, all possible transformations are performed and counted. The inclusion of all mobile species in the basis means that we have no elements in $\boldsymbol{\mathcal{R}}_{RN}$ nor in $\mathbf{R}_{RM}$. When ionic mobile species are present, we omit one of them from the set of "*A*" species, since its concentration can be found from the electro-neutrality condition. No constraint is assumed for the total pressure or concentration. Hence, no mobile species can be eliminated here by using this type of condition.

Whenever a diffusion reactor contains more than one mobile phase, the selection process just described must be done independently for each such phase. Thus, for mobile phases 1 and 2, one obtains the set $\{A^1, B^1, C^1, D^1\}$ from the stoichiometric matrix $\boldsymbol{\nu}^1$ and $\{A^2, B^2, C^2, D^2\}$ from the matrix $\boldsymbol{\nu}^2$. In addition a special set of basic species must be selected for each interface where mass transfer or reaction occurs between two mobile phases. Thus, for the interface between phases 1 and 2, one obtains the set $\{A^{12}, B^{12}, C^{12}, D^{12}, U^{12}, W^{12}\}$ from the interfacial stoichiometric matrix $\boldsymbol{\nu}^{12}$. The sets U^{12} and W^{12} form a basis of the strictly interfacial species, all of which are considered immobile in this treatment. The members of W^{12} and U^{12} are selected from equilibrium and non-equilibrium reactions, respectively. The extraction of a metal from an aqueous phase by an organic phase is an example of this type of diffusional process (Hales 1977).

The matrix $\boldsymbol{\nu}^{12}$ should include not only the interfacial reactions, but also the equilibrium reactions of each adjacent phase. However, the non-equilibrium reactions in the adjacent phases should not be included in the interfacial mass balance, since this balance is for a surface region with no associated fluid volume. In this regard, note that homogeneous reaction rates are defined per unit volume, whereas interfacial reaction rates are defined per unit area of interface.

The basic species for the interiors of the mobile phases are selected as described above. At the interface, on the other hand, we have six types of species, which must be selected by six transformations of the interfacial stoichiometric matrix $\boldsymbol{\nu}^{12}$. During the first three solution stages, all equilibrium reactions will be opened for pivot selection, and during the last three stages, all non-equilibrium reactions will be opened. The species (columns) must enter the basis in the following order: immobile interfacial species (W^{12}), immobile species (D^{12}), mobile species (B^{12}), immobile interfacial species (U^{12}), immobile species (C^{12}), and mobile species (A^{12}). The last set (A^{12}) must contain all remaining mobile species in the two phases (save one ionic mobile species from each phase that has one); hence the sixth stage can be done without matrix transformations.

FORMULATION OF LOCAL MASS BALANCES AND THERMODYNAMIC CONSTRAINTS

In this section, we formulate a set of mass balances appropriate to the selected basic "*B*," "*C*," and "*D*" species. These equations are called local, since all the unknowns in the equations have to be evaluated at the same point in space and time. Once the mobile and immobile species are designated, the local equations are formulated by the same procedure for all reactor types.

First we consider the reaction rates in the interior of a mobile phase which may contain one or more immobile species. Let the individual reaction rates per unit volume be

$$\mathcal{R}_j = k_j \left[\prod_{i=1}^{N_c} c_i^{\epsilon_{ji}} - \frac{1}{K_j} \prod_{i=1}^{N_c} c_i^{\epsilon_{ji}+\nu_{ji}} \right] \qquad j = 1, \ldots N_r \tag{33}$$

in which the ϵ_{ji} are the reaction orders for the forward rates, the ν_{ji} are the elements of the stoichiometric matrix, and c_i is the concentration or partial pressure of species i. Equations (33) require that the ν_{ji} be normalized to a single occurrence of the jth rate-controlling event, except for reactions designated as irreversible ($1/K_j = 0$) or as equilibria ($1/k_j = 0$). The production rates per unit volume for the individual species are then given formally by Equations (25) and (33). For equilibrium reactions, however, Equation (33) is not directly solvable for $\mathcal{R}_j$; rather, it provides algebraic constraints on the concentrations.

For each basic "*B*" or "*D*" species we have a local equilibrium of the form

$$\mathcal{R}_j / k_j = 0 \tag{34}$$

in which j corresponds to the pivotal row (in $\boldsymbol{\mathcal{R}}_B$ or $\boldsymbol{\mathcal{R}}_D$) for the given species in Equation (27). With this substitution, Equation (33) yields the corresponding constraints on the concentrations.

For each basic "*C*" species, the net production rate is zero at steady state:

$$\mathrm{R}_i = \sum_{j=1}^{N_r} \nu_{ji} \mathcal{R}_j = 0 \tag{35}$$

However, when equilibrium reactions are present, this form may be indeterminate. For this reason, we analyze the stoichiometric matrix once more, in transposed form, to remove the influence of the $\mathfrak{R}_B$ and $\mathfrak{R}_D$ values. After removal of the redundant fifth row (thus setting $\mathfrak{R}_{RR} = 0$), we may write Equation (26) in the transposed form

$$\begin{bmatrix} \boldsymbol{\nu}^T_{11} & \boldsymbol{\nu}^T_{21} & \boldsymbol{\nu}^T_{31} & \boldsymbol{\nu}^T_{41} & \boldsymbol{\nu}^T_{61} \\ \boldsymbol{\nu}^T_{12} & \boldsymbol{\nu}^T_{22} & \boldsymbol{\nu}^T_{32} & \boldsymbol{\nu}^T_{42} & \boldsymbol{\nu}^T_{62} \\ \boldsymbol{\nu}^T_{13} & \boldsymbol{\nu}^T_{23} & \boldsymbol{\nu}^T_{33} & \boldsymbol{\nu}^T_{43} & \boldsymbol{\nu}^T_{63} \\ \boldsymbol{\nu}^T_{14} & \boldsymbol{\nu}^T_{24} & \boldsymbol{\nu}^T_{34} & \boldsymbol{\nu}^T_{44} & \boldsymbol{\nu}^T_{64} \\ \boldsymbol{\nu}^T_{15} & \boldsymbol{\nu}^T_{25} & \boldsymbol{\nu}^T_{35} & \boldsymbol{\nu}^T_{45} & \boldsymbol{\nu}^T_{65} \\ \boldsymbol{\nu}^T_{16} & \boldsymbol{\nu}^T_{26} & \boldsymbol{\nu}^T_{36} & \boldsymbol{\nu}^T_{46} & \boldsymbol{\nu}^T_{66} \end{bmatrix} \begin{bmatrix} \mathfrak{R}_A \\ \mathfrak{R}_B \\ \mathfrak{R}_C \\ \mathfrak{R}_D \\ \mathfrak{R}_{RN} \end{bmatrix} = \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \\ \mathbf{R}_C \\ \mathbf{R}_D \\ \mathbf{R}_{RM} \\ \mathbf{R}_{RI} \end{bmatrix} \tag{36}$$

For Type II reactors all mobile species are included in the basis; hence, we combine $\mathfrak{R}_{RN}$ with $\mathfrak{R}_A$, and $\mathbf{R}_{RM}$ with $\mathbf{R}_A$ for these reactors.

The production rates, $\mathbf{R}_C$ and $\mathbf{R}_D$, of the immobile species are zero and can be added to the production rate of any other species without affecting the net result. Hence, we can solve Equation (36) for the reaction rates $\mathfrak{R}_C$ and $\mathfrak{R}_D$, without altering any of the right-hand elements. The solution for $\mathfrak{R}_C$ and $\mathfrak{R}_D$ is surely obtainable, since the previous selection of "C" and "D" species from Equation (26) guarantees that the square matrices $\boldsymbol{\nu}_{33}$ and $\boldsymbol{\nu}_{44}$ have full rank. After this transformation the matrix equation will have the form

$$\begin{bmatrix} \boldsymbol{\nu}^{T'}_{11} & \boldsymbol{\nu}^{T'}_{21} & 0 & 0 & \boldsymbol{\nu}^{T'}_{61} \\ \boldsymbol{\nu}^{T'}_{12} & \boldsymbol{\nu}^{T'}_{22} & 0 & 0 & \boldsymbol{\nu}^{T'}_{62} \\ \boldsymbol{\nu}^{T'}_{13} & 0 & \mathbf{I} & 0 & \boldsymbol{\nu}^{T'}_{63} \\ \boldsymbol{\nu}^{T'}_{14} & \boldsymbol{\nu}^{T'}_{24} & 0 & \mathbf{I} & \boldsymbol{\nu}^{T'}_{64} \\ \boldsymbol{\nu}^{T'}_{15} & \boldsymbol{\nu}^{T'}_{25} & 0 & 0 & \boldsymbol{\nu}^{T'}_{65} \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \mathfrak{R}_A \\ \mathfrak{R}_B \\ \mathfrak{R}_C \\ \mathfrak{R}_D \\ \mathfrak{R}_{RN} \end{bmatrix} = \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \\ \mathbf{R}_C \\ \mathbf{R}_D \\ \mathbf{R}_{RM} \\ \mathbf{R}_{RI} \end{bmatrix} \tag{37}$$

The coefficients in $\boldsymbol{\nu}^{T'}_{23}$ have also vanished. This happens because the "D" species were originally selected prior to the "B" species. Hence, the production rates of the "C" species take the form

$$\mathbf{R}_C = \boldsymbol{\nu}^{T'}_{13}\mathfrak{R}_A + \mathfrak{R}_C + \boldsymbol{\nu}^{T'}_{63}\mathfrak{R}_{RN} \tag{38}$$

independent of the indeterminate quantities $\mathfrak{R}_B$ and $\mathfrak{R}_D$. Thus, instead of using Equation (35) to express the immobility constraints, we use Equation (38) with $\mathbf{R}_C = 0$. The coefficient matrix in Equation (37) is called the reduced stoichiometric matrix.

For adiabatic reactors of Type I with given initial conditions, we may also calculate the temperature as a function of the local extents, from an energy balance and a thermal equation of state.

Equations (33)-(38) will also hold at an interface between two mobile phases in a diffusion reactor, if the sets of "C" and "D" species are extended to include all basic "U" and "W" species, respectively.

This completes the local equations necessary for the determination of the temperature and the concentrations of the "B," "C," and "D" species, in terms of the local concentrations of the basic "A" species. Note that the basic "B" species, although designated as mobile, give rise only to local equations of thermodynamic equilibrium (see Equation (34)).

FORMULATION OF SPATIAL MASS BALANCES FOR TYPE I REACTORS

In this section we formulate a set of combined mass balances for the basic "A" and "B" species. These equations are called spatial since the variables in the equations are evaluated at more than one point in space or time. The total number of spatial mass balances must be equal to the number of basic "A" species, but we have to construct a set of combined mass balances to remove indeterminacy whenever any "B" species are present. A plug flow reactor at steady state is considered for illustration.

For the basic mobile species, we may formally write the following mass-balance equations, obtained from Equation (37) with $\mathbf{R}_C$ and $\mathbf{R}_D$ set equal to zero:

$$\frac{F}{V}\frac{d}{dx}\begin{bmatrix} \boldsymbol{\xi}_A \\ \boldsymbol{\xi}_B \end{bmatrix} = \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \end{bmatrix} = \begin{bmatrix} \boldsymbol{\nu}^{T'}_{11} & \boldsymbol{\nu}^{T'}_{21} & \boldsymbol{\nu}^{T'}_{61} \\ \boldsymbol{\nu}^{T'}_{12} & \boldsymbol{\nu}^{T'}_{22} & \boldsymbol{\nu}^{T'}_{62} \end{bmatrix} \begin{bmatrix} \mathfrak{R}_A \\ \mathfrak{R}_B \\ \mathfrak{R}_{RN} \end{bmatrix} \tag{39}$$

Here V is the reactor volume, F the feed rate, and $\boldsymbol{\xi}$ the set of extents of production. Even though $\mathbf{R}_A$ is based on the stoichiometry of Equation (37) rather than (36), it may still include indeterminate rate expressions ($\mathfrak{R}_B$) if $\boldsymbol{\nu}^{T'}_{21}$ is non-zero.

Equations (39) are now combined to obtain a subset of new equations in which the influence of $\mathfrak{R}_B$ does not appear. The second part of Equation (39) is first rewritten as

$$\begin{bmatrix} \mathbf{I} & 0 \\ 0 & \mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \end{bmatrix} = \begin{bmatrix} \boldsymbol{\nu}^{T'}_{11} & \boldsymbol{\nu}^{T'}_{21} & \boldsymbol{\nu}^{T'}_{61} \\ \boldsymbol{\nu}^{T'}_{12} & \boldsymbol{\nu}^{T'}_{22} & \boldsymbol{\nu}^{T'}_{62} \end{bmatrix} \begin{bmatrix} \mathfrak{R}_A \\ \mathfrak{R}_B \\ \mathfrak{R}_{RN} \end{bmatrix} \tag{40}$$

Elimination of $\mathfrak{R}_B$ from the upper row by Gauss-Jordan row operations then gives

$$\begin{bmatrix} \mathbf{I} & \boldsymbol{\beta}_A \\ 0 & \boldsymbol{\nu}_0 \end{bmatrix} \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \end{bmatrix} = \begin{bmatrix} \boldsymbol{\nu}^{T''}_{11} & 0 & \boldsymbol{\nu}^{T''}_{61} \\ \boldsymbol{\nu}^{T''}_{12} & \mathbf{I} & \boldsymbol{\nu}^{T''}_{62} \end{bmatrix} \begin{bmatrix} \mathfrak{R}_A \\ \mathfrak{R}_B \\ \mathfrak{R}_{RN} \end{bmatrix} \tag{41}$$

The selection of the "B" species prior to the "A" species in the solution of Equation (26) guarantees that $\boldsymbol{\nu}^{T'}_{22}$ has full rank. Equation (41) demonstrates that the vector $\mathbf{R}_A + \boldsymbol{\beta}_A\mathbf{R}_B$ can be calculated directly from non-equilibrium reaction rates $\mathfrak{R}_A$ and $\mathfrak{R}_{RN}$. Hence, the following combined mass balances on the "A" and "B" species

$$\frac{F}{V}\frac{d}{dx}\begin{bmatrix} \mathbf{I} & \boldsymbol{\beta}_A \end{bmatrix} \begin{bmatrix} \boldsymbol{\xi}_A \\ \boldsymbol{\xi}_B \end{bmatrix} = \begin{bmatrix} \mathbf{I} & \boldsymbol{\beta}_A \end{bmatrix} \begin{bmatrix} \mathbf{R}_A \\ \mathbf{R}_B \end{bmatrix} \tag{42}$$

give the correct number of independent spatial mass balances. Here $\mathbf{R}$ must be calculated from the reduced stoichiometric matrix obtained in Equation (37). Note that the combinations in Equation (42) are developed independently of the elemental compositions of the species. In actual calculations, the transformation of $\boldsymbol{\nu}^{T'}_{11}$, $\boldsymbol{\nu}^{T'}_{12}$, $\boldsymbol{\nu}^{T'}_{61}$, and $\boldsymbol{\nu}^{T'}_{62}$ is not needed to obtain $\boldsymbol{\beta}_A$; we need only transform $\boldsymbol{\nu}^{T'}_{21}$ and $\boldsymbol{\nu}^{T'}_{22}$.

For Type I reactors that are neither isothermal nor adiabatic we must also add a spatial energy balance and a thermal equation of state to obtain the temperature profile.

This completes the formulation for Type I reactors, except that the initial conditions must, of course, be stated.

FORMULATION OF SPATIAL MASS BALANCES FOR TYPE II REACTORS

The steady-state equations for the interior part of a non-flow diffusion reactor are similar to those for the plug-flow reactor, except that the forced convection term $(F/V)\ \nabla\boldsymbol{\xi}$ is replaced by a diffusion term $\nabla \bullet (\mathbf{D}\ \nabla\mathbf{C})$; the total diffusivity matrix $\mathbf{D}$ may be a function of all concentrations. Whenever ionic mobile species are present, we must also include a spatial mass balance equation for the one ionic mobile species excluded from the list of basic species, and include the electrical potential as a dependent variable.

A major difference between Type I and Type II reactors appears at the interfaces between the mobile phases. For the mobile species, we may formally write the following boundary conditions (interfacial mass balance equations)

$$\begin{bmatrix} \mathbf{N}_{A12} \\ \mathbf{N}_{B12} \end{bmatrix} = \begin{bmatrix} \mathbf{R}_{A12} \\ \mathbf{R}_{B12} \end{bmatrix} = \begin{pmatrix} \boldsymbol{\nu}_{11}^{T'} & \boldsymbol{\nu}_{21}^{T'} \\ \boldsymbol{\nu}_{12}^{T'} & \boldsymbol{\nu}_{22}^{T'} \end{pmatrix} \begin{bmatrix} \boldsymbol{\mathcal{R}}_{A12} \\ \boldsymbol{\mathcal{R}}_{B12} \end{bmatrix} \tag{43}$$

Here $\mathbf{N}$ is the vector of interfacial molar fluxes of all basic mobile species, measured into the relevant phase for each. $\mathbf{R}$ and $\boldsymbol{\mathcal{R}}$ are the corresponding vectors of interfacial production and reaction rates, related as shown by an interfacial stoichiometric matrix. As mentioned before, no distinction is now made between $\boldsymbol{\mathcal{R}}_A$ and $\boldsymbol{\mathcal{R}}_{RN}$ in Equation (36); here we include all those reactions in $\boldsymbol{\mathcal{R}}_A$. These boundary conditions are spatial equations, since the flux expressions involve the concentration gradients in the adjoining phases.

These equations are transformed to give a subset of boundary conditions in which the indeterminate quantities $\boldsymbol{\mathcal{R}}_{B12}$ do not appear. The transformation is similar to that for Equations (40) and (41); the result may be written

$$[\mathbf{I} \quad \boldsymbol{\beta}_{A12}] \begin{bmatrix} \mathbf{N}_{A12} \\ \mathbf{N}_{B12} \end{bmatrix} = [\mathbf{I} \quad \boldsymbol{\beta}_{A12}] \begin{bmatrix} \mathbf{R}_{A12} \\ \mathbf{R}_{B12} \end{bmatrix} = \boldsymbol{\nu}_{11}^{T''} \boldsymbol{\mathcal{R}}_{A12} \tag{44}$$

The number of equations here is equal to the total number of species in the set A^{12}. The interfacial reaction equilibria and kinetic expressions automatically provide the appropriate boundary conditions on the concentrations.

For a non-isothermal diffusion reactor, an interfacial energy balance must also be formulated, as a boundary condition on the energy flux. The temperature may be treated as continuous across the interface.

When ionic mobile species are present, boundary conditions for the electrical potential become necessary. At the first boundary, we may specify a fixed potential; no dependent variable and no spatial equation arise from this kind of condition. If another boundary is present, we must specify 1) the potential, 2) the current, or 3) a relation involving the two at the second boundary. In the cases 2 and 3, we must add one more spatial equation (a relation between the mass fluxes and the total current) and one more dependent variable (the boundary potential) to the set of spatial equations.

EXAMPLE 3

This example demonstrates the selection of basic "*A*," "*B*," "*C*," and "*D*" species, and the construction of corresponding mass balances and thermodynamic constraints for a Type I reactor.

Consider a reaction network with six species and four reversible reactions. Let species {3, 4, 5} belong to an immobile catalytic phase, and let the first two reactions be at equilibrium:

$$P_1 + S_3 = S_4 + P_2$$
$$P_2 + S_3 = S_4$$
$$P_2 + S_4 \rightleftharpoons S_5$$
$$S_5 \rightleftharpoons S_3 + P_6$$

Here the P_i may be gas-phase species, and the S_i may be active catalytic surface species.

We wish to formulate a set of equations for a steady-state simulation of this reaction network in an isothermal plug-flow reactor. The stoichiometric matrix $\boldsymbol{\nu}$ for the system is

$$\begin{array}{c|cccccc|} & P_1 & P_2 & S_3 & S_4 & S_5 & P_6 \\ \hline 1 & -1 & 1 & -1 & 1 & & \\ 2 & & -1 & -1 & 1 & & \\ 3 & & -1 & & -1 & 1 & \\ 4 & & & 1 & & -1 & 1 \\ \hline \end{array}$$

To obtain the basic species, we transform this matrix. During the first stage we open columns {3, 4, 5} and rows {1, 2} for pivot selection. This allows one transformation, giving

$$\begin{array}{c|cccccc|} & 1 & 2 & 3D & 4 & 5 & 6 \\ \hline 1D & 1 & -1 & 1 & -1 & & \\ 2 & 1 & -2 & & & & \\ 3 & & -1 & & -1 & 1 & \\ 4 & -1 & 1 & & 1 & -1 & 1 \\ \hline \end{array}$$

in which species 3 becomes a "*D*" species. During the second stage we also open columns {1, 2, 6}. This allows one more transformation, giving

$$\begin{array}{c|cccccc|} & 1B & 2 & 3D & 4 & 5 & 6 \\ \hline 1D & & 1 & 1 & -1 & & \\ 2B & 1 & -2 & & & & \\ 3 & & -1 & & -1 & 1 & \\ 4 & & -1 & & 1 & -1 & 1 \\ \hline \end{array}$$

in which species 1 becomes a "*B*" species. During the third stage we open columns {4, 5} and rows {3, 4} for pivot selection. This allows one transformation, giving

$$\begin{array}{c|cccccc|} & 1B & 2 & 3D & 4C & 5 & 6 \\ \hline 1D & & 2 & 1 & & -1 & \\ 2B & 1 & -2 & & & & \\ 3C & & 1 & & 1 & -1 & \\ 4 & & -2 & & & & 1 \\ \hline \end{array}$$

in which species 4 becomes a "*C*" species. During the fourth stage we open also columns {2, 6} and perform one final transformation, giving

$$\begin{array}{c|cccccc|}
 & 1B & 2A & 3D & 4C & 5 & 6 \\
\hline
1D & & & 1 & & -1 & 1 \\
2B & 1 & & & & & -1 \\
3C & & & & 1 & -1 & 0.5 \\
4A & & 1 & & & & -0.5 \\
\hline
\end{array}$$

which completes the stoichiometric basis, with species 2 as an "*A*" species. This array gives the following relations for the non-basic species when inserted into Equations (31) and (32):

$$\xi_5 = -\xi_3 - \xi_4$$

$$\xi_6 = -\xi_1 - 0.5\xi_2$$

The extents ξ_3, ξ_4, and ξ_5 represent changes in the catalytic surface concentrations from their initial values.

Next, we select the appropriate combinations of production rates. We start again with the original stoichiometric matrix (transposed as in Equation (36)) and open columns {3, 4} and rows {1, 3} for pivot selection. The following reduced stoichiometric matrix (transposed as in Equation (37)) is obtained after two transformations:

$$\begin{array}{c|cccc|}
 & 1D & 2 & 3C & 4 \\
\hline
1 & & 1 & & -1 \\
2 & & -2 & & \\
3D & 1 & 1 & & -1 \\
4C & & & 1 & -1 \\
5 & & & & \\
6 & & & & 1 \\
\hline
\end{array}$$

Note that the production rate of species 4 now is free of both equilibrium reactions as indicated in row *C* of Equation (37).

We are now ready to formulate the various mass balances and thermodynamic constraints. For each "*B*" and "*D*" species we have a local thermodynamic constraint:

$$\mathcal{R}_1/k_1 = 0$$

$$\mathcal{R}_2/k_2 = 0$$

For the "*C*" species we have a local steady-state condition,

$$R_4 = \mathcal{R}_3 - \mathcal{R}_4 = 0$$

obtainable from the fourth row of the matrix just given.

The one "*A*" species requires one spatial mass balance. To construct this we calculate the $\boldsymbol{\beta}$ matrix of Equation (41) by first extracting the "*A*" and "*B*" elements from the *B* column of the reduced stoichiometric matrix (i.e., the elements in rows 2 and 1 of column 2):

$$\begin{pmatrix} \boldsymbol{\nu}^{T'}_{21} \\ \boldsymbol{\nu}^{T'}_{22} \end{pmatrix} = \begin{bmatrix} -2 \\ 1 \end{bmatrix}$$

Then we combine this matrix with a null and a unit matrix

$$\begin{pmatrix} \mathbf{0} & \boldsymbol{\nu}^{T'}_{21} \\ \mathbf{I} & \boldsymbol{\nu}^{T'}_{22} \end{pmatrix} = \begin{bmatrix} 0 & -2 \\ 1 & 1 \end{bmatrix}$$

and finally eliminate $\boldsymbol{\nu}^{T'}_{21}$ with $\boldsymbol{\nu}^{T'}_{22}$ as pivot

$$\begin{bmatrix} \boldsymbol{\beta} & \mathbf{0} \\ \boldsymbol{\nu}_0 & \mathbf{I} \end{bmatrix} = \begin{bmatrix} 2 & 0 \\ 1 & 1 \end{bmatrix}$$

Hence $\boldsymbol{\beta}$ is a one-element matrix with the value 2, and the spatial mass balance becomes, according to Equations (41) and (42)

$$\frac{F}{V}\left[\frac{d\xi_2}{dx} + 2\frac{d\xi_1}{dx}\right] = R_2 + 2R_1$$

$$= -2\mathcal{R}_2 + 2(\mathcal{R}_2 - \mathcal{R}_4) = -2\mathcal{R}_4$$

This is the final equation; however by use of the stoichiometric relationship for ξ_6 we could rewrite this mass balance in the form

$$\frac{F}{V}\frac{d\xi_6}{dx} = \mathcal{R}_4$$

which could have been constructed intuitively from reaction 4 for this simple reaction scheme.

Note that the mass balances on surface species are formed directly from the stoichiometry, whatever the number of kinds of active sites. As mentioned earlier, no information about the elemental compositions of the species is required (once the stoichiometric coefficients ν_{ji} are correctly assigned).

EXAMPLE 4

This example demonstrates the selection of basic "*A*" and "*B*" species, the construction of corresponding mass-balances and thermodynamic constraints, and particularly the determination of the $\boldsymbol{\beta}$ matrix.

Consider a one-dimensional film of aqueous electrolyte with nine species and four homogeneous equilibrium reactions (Hales 1977)

$$Cu^{++} + H_2O = Cu(OH)^+ + H^+$$

$$H^+ + OH^- = H_2O$$

$$Cu^{++} + SO_4^{--} = CuSO_4$$

$$H^+ + SO_4^{--} = HSO_4^-$$

In addition the mobile phase contains Na^+. We number the species as follows: (1) Cu^{++}, (2) $Cu(OH)^+$, (3) $CuSO_4$, (4) SO_4^{--}, (5) HSO_4^-, (6) Na^+, (7) H^+, (8) OH^-, and (9) H_2O. The stoichiometric matrix $\boldsymbol{\nu}$ for this system is

$$\begin{array}{c|ccccccccc|}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\
\hline
1 & -1 & 1 & & & & & 1 & & -1 \\
2 & & & & & & & -1 & -1 & 1 \\
3 & -1 & & 1 & -1 & & & & & \\
4 & & & & -1 & 1 & & -1 & & \\
\hline
\end{array}$$

To obtain the basic species, we transform this matrix. First we select component 4 to be computed from the electroneutrality condition. All species are mobile; hence no basic species can be selected during the first Gauss-Jordan elimination. During the second stage, we open all columns (except column 4) and all rows for pivot selection, and obtain after four eliminations

$$\begin{array}{c|ccccccccc|}
 & 1B & 2B & 3 & 4 & 5 & 6 & 7B & 8B & 9 \\
\hline
1B & 1 & & -1 & 1 & & & & & \\
2B & & & & 1 & -1 & & 1 & & \\
3B & & 1 & -1 & & 1 & & & & -1 \\
4B & & & & -1 & 1 & & & 1 & -1 \\
\hline
\end{array}$$

No basic species are selected during stage three. During stage four, we select all remaining species (except SO_4^{--}) as basic "*A*" species without further transformations.

Hence, the "*A*" species are {3, 5, 6, 9} and the "*B*" species are {1, 2, 7, 8}. The concentrations of these eight species must be used as dependent variables, together with the electrical potential. The concentration of SO_4^{--} is obtained from the electro-neutrality condition

$$2c_4 = 2c_1 + c_2 - c_5 + c_6 + c_7 - c_8$$

There is no need for the reduced stoichiometric matrix since no immobile species are present. However, we need the β matrix to obtain the spatial mass balances.

First, we construct the following matrix in which the left part consists of a null and a unit matrix, and the right part consists of the reordered and transposed stoichiometric matrix:

$$\begin{array}{c|cccc|cccc|}
 & 1B & 2B & 7B & 8B & 1 & 2 & 3 & 4 \\
\hline
3A & & & & & & & 1 & \\
4 & & & & & & & -1 & -1 \\
5A & & & & & & & & 1 \\
6A & & & & & & & & \\
9A & & & & & -1 & 1 & & \\
\hline
1B & 1 & & & & -1 & & -1 & \\
2B & & 1 & & & 1 & & & \\
7B & & & 1 & & 1 & -1 & & -1 \\
8B & & & & 1 & & -1 & & \\
\hline
\end{array}$$

Next, we eliminate all elements in the upper right-hand rectangle. Once these four eliminations are done we obtain

$$\begin{array}{c|cccc|cccc|}
 & 1B & 2B & 7B & 8B & 1 & 2 & 3 & 4 \\
\hline
3A & 1 & 1 & & & & & & \\
4 & -1 & & -1 & 1 & & & & \\
5A & & -1 & 1 & -1 & & & & \\
6A & & & & & & & & \\
9A & & 1 & & 1 & & & & \\
\hline
1B & -1 & -1 & & & & & 1 & \\
2B & & 1 & & & 1 & & & \\
7B & & 1 & -1 & 1 & & & & 1 \\
8B & & & & -1 & & 1 & & \\
\hline
\end{array}$$

in which the upper left-hand array is the β matrix.

Since we have four "*B*" species, we can formulate four local equilibrium equations

$$\mathcal{R}_1/k_1 = 0 \qquad \mathcal{R}_2/k_2 = 0$$

$$\mathcal{R}_3/k_3 = 0 \qquad \mathcal{R}_4/k_4 = 0$$

The remaining "*A*" species and species 4 require five spatial differential equations. At steady state, these take the form

$$(\nabla \bullet [N_3 + N_1 + N_2]) = R_3 + R_1 + R_2 = 0$$

The first part of this equation is found from the first row in the **I** and β matrices, and the second part is found from columns {1, 2, 3} of the stoichiometric matrix. Similarly, from the remaining four rows of the **I** and β matrices we find

$$(\nabla \bullet [N_4 - N_1 - N_7 + N_8]) = R_4 - R_1 - R_7 + R_8 = 0$$

$$(\nabla \bullet [N_5 - N_2 + N_7 - N_8]) = R_5 - R_2 + R_7 - R_8 = 0$$

$$(\nabla \bullet [N_6)] = R_6 = 0$$

$$(\nabla \bullet [N_9 + N_2 + N_8]) = R_9 + R_2 + R_8 = 0$$

The molar fluxes N_i may be expressed in terms of the velocity and the gradients of concentration and electrical potential (Newman 1973). This completes the construction of the mass balances.

Here the first and last spatial equations may be considered as mass balances for total Cu and for OH^-. The remaining three equations are combinations of other mass balances. Note, however, that no use of the elemental compositions of the species was made in setting up these equations.

ACKNOWLEDGMENT

This work was supported by Grant ENG 76-24368 of the National Science Foundation, and by the University of Wisconsin-Madison Graduate School Research Committee.

LITERATURE CITED

Aris, R. and R. H. S. Mah, "Independence of Chemical Reactions," *Ind. Eng. Chem. Fundam.*, **2**, 90 (1963).

Aris, R., *Elementary Chemical Reactor Analysis*, Prentice-Hall, Englewood Cliffs, NJ (1969).

Beek, J., "Design of Packed Catalytic Reactors," *Adv. Chem. Eng.*, 3, 203 (1962).

Guertin, E. W., J. P. Sørensen, and W. E. Stewart, "Exponential Collocation of Stiff Reactor Models," *Comp. Chem. Eng.*, **1**, 197 (1977).

Hales, C. H., "The Effect of Bulk Concentration Parameters on Liquid-Liquid Extraction of Copper with Sodium Loaded Di-(2-Ethylhexyl) Phosphoric Acid," M.S. thesis, University of Wisconsin, Madison (1977).

Hildebrand, F. B., *Methods of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1952).

Isaacson, E. and H. B. Keller, *Analysis of Numerical Methods*, Wiley, New York (1966).

Newman, J., *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ (1973).

Prater, C. D., A. J. Silvestri, and J. Wei, "On the Structure and Analysis of Complex Systems of First Order Chemical Reactions Containing Irreversible Steps, I. General Properties," *Chem. Eng. Sci.*, **22**, 1587 (1967).

Schneider, D. R. and G. V. Reklaitis, "On Material Balances for Chemically Reacting Systems," *Chem. Eng. Sci.*, **30**, 243 (1975).

Schubert, E. and H. Hofmann, "Reaction Engineering, 1. Stoichiometry of Complex Reactions," *International Chem. Eng.*, **16**, 132 (1976).

Schultz, J. S., J. D. Goddard, and S. R. Suchdeo, "Facilitated Transport via Carrier Mediated Diffusion in Membranes," *AIChE J.*, **20**, 417, 625 (1974).

Stewart, W. E. and J. P. Sørensen, "Sensitivity and Regression of Multicomponent Reactor Models," Fourth International Symposium on Chemical Reaction Engineering, Heidelberg (1976).

Whitwell, J. C. and S. R. Dartt, "Independent Reactions in the Presence of Isomers," *AIChE J.*, **19**, 1114 (1973).

Manuscript received October 14, 1977; revision received June 28, and accepted July 9, 1979.