Local, Global, and Elementary Stoichiometry

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DOI 10.1002/aic.12593
Published online May 6, 2011 in Wiley Online Library (wileyonlinelibrary.com).

Stoichiometry refers to conservation of atomic species. In this article, local refers to a point at the continuum level, global refers to the macroscopic balance level, and elementary refers to conservation of atomic species associated with distinct kinetic steps. The role of stoichiometry in the determination of the pivot matrix and the mechanistic matrix is presented. The elements of both these matrices are referred to as stoichiometric coefficients; however, both sets of coefficients are different and both play different roles in the analysis of chemical reactors. © 2011 American Institute of Chemical Engineers AIChE J., 58: 538–552, 2012

Keywords: reactor analysis, reaction kinetics

Introduction

Aris1 describes stoichiometry as the bookkeeping of atomic species. This bookkeeping goes hand-in-hand with the axiom for conservation of mass that we state as

Axiom I:
\[ \frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A v_A) = r_A, \quad A = 1, 2, \ldots, N \quad (1) \]

Here \( \rho_A \) is the mass density of species \( A \), while \( v_A \) is the velocity of species \( A \) and \( r_A \) is the net mass rate of production of species \( A \) owing to chemical reaction. The fact that mass is neither created nor destroyed by chemical reaction is expressed as

Axiom II:
\[ \sum_{A=1}^{A=N} r_A = 0 \quad (2) \]

In this representation, we have used \( N \) to signify the number of stable, identifiable species. In any chemical reaction there are molecular fragments and active species that exist only in small amounts, and the precise nature and amount of these fragments are generally unknown. Hidden behind the statement made by Eq. 2 is the assumption that what is unknown and undetectable does not play a significant role in the concept of conservation of mass.

When dealing with chemical reactions, the molar forms of Axioms I and II are preferred and the first of these is given by

Axiom I:
\[ \frac{\partial c_A}{\partial t} + \nabla \cdot (c_A v_A) = R_A, \quad A = 1, 2, \ldots, N \quad (3) \]

Here, we have used
\[ c_A = \frac{\rho_A}{M W_A}, \quad R_A = \frac{r_A}{M W_A} \quad (4) \]
in which \( M W_A \) represents the molecular mass of species \( A \). The fact that mass is neither created nor destroyed by chemical reaction can also be expressed as

Axiom II:
\[ \sum_{A=1}^{A=N} M W_A R_A = 0 \quad (5) \]

Here, it is important to recognize that \( R_A \) has the meaning

\[ R_A = \begin{cases} \text{net molar rate of production per unit volume of species } A \\ \text{owing to chemical reactions} \end{cases} \quad (6) \]

which can also be interpreted as
\[ R_A = \begin{cases} \text{molar rate of creation of} \\
\text{species } A \text{ per unit volume} \\
\text{owing to chemical reactions} \end{cases} \]

\[ - \begin{cases} \text{molar rate of consumption of} \\
\text{species } A \text{ per unit volume} \\
\text{owing to chemical reactions} \end{cases} \] (7)

Clearly Eqs. 6 and 7 are equivalent descriptions of \( R_A \), thus, the reader is free to choose which ever set of words is most appealing. In this article, we will use the phrase "net rate of production" to describe quantities such as \( R_A, R_B \), and so forth.

**Local Stoichiometry**

To be precise about the role of "atomic species" in the principle of conservation of mass during chemical reactions, we explore an alternative representation of Axiom II given by

Axion II: \[ \begin{cases} \text{the molar rate of production} \\
\text{per unit volume of } J\text{-type atoms} \\
\text{owing to chemical reactions} \end{cases} = 0 \]

\[ J = 1, 2, ..., T, \] (8)

in which we have used \( T \) to represent the number of atomic species. From this statement of Axiom II, we need to extract a "mathematical equation," and to do this we define the number \( N_{JA} \) as

\[ N_{JA} = \begin{cases} \text{number of moles} \\
\text{of } J\text{-type atoms per} \\
\text{mole of species } A \end{cases} \\
J = 1, 2, ..., T \text{ and } A = 1, 2, ..., N \] (9)

A little thought will indicate that the product of \( N_{JA} \) and \( R_A \) can be described as

\[ N_{JA} R_A = \begin{cases} \text{net molar rate of production per unit} \\
\text{volume of } J\text{-type atoms owing to the} \\
\text{net molar rate of production of species } A \end{cases} \] (10)

and the axiomatic statement given by Eq. 8 takes the form

Axion II: \[ \sum_{A = 1}^{N} N_{JA} R_A = 0, \quad J = 1, 2, ..., T \] (11)

We refer to \( N_{JA} \) as the "atomic species indicator," and we identify the array of coefficients associated with \( N_{JA} \) as the "atomic matrix." Here, we note that Axiom II has been identified by Eqs. 2, 5, 8 and 11, and this is acceptable because each one of these representations can be derived from the others. The earliest reference that the authors have found for Eq. 11 is given by Eq. 159A.3 of Truesdell and Toupin.

If we make use of the atomic matrix and the "column matrix of the net rates of production," we can express Axiom II as

\[
\begin{bmatrix}
N_{11} & N_{12} & N_{13} & \cdots & N_{1,N-1} & N_{1N} \\
N_{21} & N_{22} & N_{23} & \cdots & N_{2,N-1} & N_{2N} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
N_{T1} & N_{T2} & N_{T3} & \cdots & N_{T,N-1} & N_{TN} \\
\end{bmatrix}
\begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
\vdots \\
R_N-1 \\
R_N \\
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0 \\
\vdots \\
0 \\
\end{bmatrix}
\] (12)

and in terms of compact notation this takes the form

\[ AR = 0 \] (13)

Although this equation provides a clear statement about conservation of atomic species, we need to transform this result to obtain the "pivot theorem." We begin this analysis with the idea that the atomic matrix can always be expressed in row reduced echelon form, and a uniqueness proof is given in Section 3.8 of Noble. This means that we can use a series of "elementary row operations" and column/row operations to express Eq. 12 in the form

\[
\begin{bmatrix}
1 & 0 & 0 & \cdots & 0 & \bar{N}_{1,T+1} & \cdots & \bar{N}_{1N} \\
0 & 1 & 0 & \cdots & 0 & \bar{N}_{2N} \\
0 & 0 & 1 & \cdots & 0 & \bar{N}_{2N} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 1 & \bar{N}_{W+1,T} & \cdots & \bar{N}_{W,N} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
\vdots \\
R_N \\
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0 \\
\vdots \\
0 \\
\end{bmatrix}
\] (14)

Here, we see that we have \( W \) rows of nonzero values and \( T - W \) rows of zeros. This indicates that the rank of the atomic matrix is \( r = \text{rank} = W \) and that we have \( T - W \) linearly dependent equations in the set of \( T \) equations. As the row rank and the column rank must be the same, we have \( N = W \) linearly dependent columns. The rank of the atomic matrix may be less than \( T \) when two or more rows of the atomic
matrix are a linear combination of each other. This occurs if two or more atomic elements appear in each molecular species in the same ratio. For example, in a system containing benzene \((C_6H_6)\) and acetylene \((C_2H_2)\) the atomic matrix has \(r = rank = 1\) with \(T = 2\). In compact notation we express Eq. 14 as

\[
A^* R = 0
\]  
(15)

in which \(A^*\) is the row reduced echelon form of the atomic matrix.

The form of the atomic matrix given in Eq. 14 is crucial to the efficient application of Axiom II, and this form is “not universally identified” as the “row reduced echelon form.” Sometimes one encounters the following definition of a row reduced echelon matrix:

1. The first nonzero element in any nonzero row is 1 (called a “leading 1”).
2. The leading 1 in each nonzero row appears in a column in which every other element is 0.
3. In any two successive rows with nonzero elements, the leading 1 of the lower row occurs farther to the right than the leading 1 of the higher row.
4. Rows containing only zero elements are grouped together at the bottom.

An example of an atomic matrix having these particular characteristics is the following:

\[
A = \begin{bmatrix}
1 & 2 & 0 & 3 & 0 & 4 & 0 & 5 \\
0 & 0 & 1 & 7 & 0 & 8 & 0 & 9 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]  
(16)

and we refer to this as simply a “row reduced form.”

In the atomic matrix, one can interchange columns without affecting the result as long as the attendant rows of \(R\) are also interchanged. In terms of Eq. 11, this column/row interchange is expressed as

\[
N_{JP}R_P \leftarrow N_{JP}R_P. \quad B, D = 1, 2, ..., N \text{ and } J = 1, 2, ..., T
\]  
(17)

Returning to Eq. 16, we follow this rule and interchange column #2 with column #3 to obtain

\[
C2 \leftrightarrow C3: \quad A' = \begin{bmatrix}
1 & 0 & 2 & 3 & 0 & 4 & 0 & 5 \\
0 & 1 & 0 & 7 & 0 & 8 & 0 & 9 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]  
(18)

We can now interchange column #3 with column #7 to provide

\[
C3 \leftrightarrow C7: \quad A'' = \begin{bmatrix}
1 & 0 & 0 & 3 & 0 & 4 & 2 & 5 \\
0 & 1 & 0 & 7 & 0 & 8 & 0 & 9 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{bmatrix}
\]  
(19)

which is the author’s version of a “row reduced echelon form.”

This form follows directly if we replace Statement #3 in the above definition of the row reduced echelon form with

3. In any two successive rows with non-zero elements, the leading 1 of the lower row occurs one column to the right of the leading 1 of the higher row.

At this point, we return to Eq. 14, ignore the rows of zeros, and make use of a row/column partition to obtain

\[
\begin{bmatrix}
1 & 0 & 0 & \ldots & 0 & N_{i,T-1} & \ldots & N_{iT} \\
0 & 1 & 0 & \ldots & 0 & \ldots & N_{2T} \\
0 & 0 & 1 & \ldots & 0 & \ldots & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & 0 & 0 & 1 & N_{NT-1} & \ldots & N_{NT} \\
\end{bmatrix} \begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
\ldots \\
R_T \\
R_{T-1} \\
R_N \\
\end{bmatrix} = \begin{bmatrix}
0 \\
0 \\
0 \\
\ldots \\
0 \\
0 \\
0 \\
\end{bmatrix}
\]  
(20)

In compact notation, this can be expressed as

\[
\begin{bmatrix}
I & W \\
W^T & R_P \\
\end{bmatrix} \begin{bmatrix}
R_{NP} \\
R_P \\
\end{bmatrix} = \begin{bmatrix}
0 \\
0 \\
\end{bmatrix}
\]  
(21)

Here, \(I\) represents the \((T - W) \times (T - W)\) identity matrix, \(W\) represents the \(W \times [N - (T - 1)]\) matrix of coefficients, \(R_{NP}\) represents the “nonpivot species” column matrix of net rates of production, and \(R_P\) represents the “pivot species” column matrix of net rates of production. Carrying out the matrix multiplication in Eq. 21 leads to

\[
IR_{NP} + WR_P = 0
\]  
(22)

We now define the pivot matrix as

\[
P = -W
\]

to obtain the pivot theorem given by

Pivot Theorem: \(R_{NP} = P R_P\)

Although Eqs. 2, 5, 11, and 12 often provide useful information, it is the pivot theorem that represents the most important result one can obtain from Axiom II. In the development of the pivot theorem, the choice of pivot and nonpivot species is not arbitrary. To obtain the row reduced echelon form indicated by Eq. 14, it is a necessary condition that all the atomic species be present in at least one nonpivot species. This condition can be achieved by the initial arrangement of the atomic matrix or by the operations indicated in Eq. 17.

When dealing with single independent reactions, such as the complete combustion of ethane by “homogeneous reaction” with oxygen illustrated in Figure 1, one can “balance” the chemical reaction in terms of a “picture” by counting atoms to obtain

\[
\frac{1}{2}C_2H_6 + \frac{7}{2}O_2 \rightarrow \frac{3}{2}H_2O + CO_2
\]  
(24)

From this picture one must deduce the equations that are necessary to solve problems. With a little intuitive thought one can construct “constraints” on the net rates of production given by

\[
R_{C_2H_6} = -\frac{1}{2}R_{CO_2}, \quad R_O_2 = -\frac{3}{4}R_{C_2H_6}, \quad R_{H_2O} = -\frac{3}{2}R_{CO_2}
\]  
(25)
However, one intuitive solution may not be the same as another intuitive solution, and sometimes the coefficients in this set of equations get reversed and a significant error occurs. Use of Eq. 23 to obtain Eqs. 25 avoids this possibility.

We now move beyond the single independent “homogeneous reaction” suggested by Figure 1, and consider the catalytic oxidation of ethane to produce ethylene (C2H4) and acetic acid (CH3COOH) along with carbon dioxide (CO2), carbon monoxide (CO), and water (H2O). This situation is illustrated in Figure 2 where we have suggested that a “heterogeneous reaction” occurs at the γ-κ interface. In reality the reaction mechanism will be much more complex than suggested in Figure 2 where we wish only to emphasize that the reaction occurs at a fluid-solid interface. In Appendix A, we show that both homogeneous and heterogeneous reactions can be treated within a single framework.

Given the two reactants and the five products illustrated in Figure 2, one might count atoms to obtain:

\[
3\text{C}_2\text{H}_6 + 5\text{O}_2 \rightarrow \text{CO}_2 + \text{CO} + 5\text{H}_2\text{O} + \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH}
\]  
(26)

However, one could also count atoms to develop a different result given by

\[
4\text{C}_2\text{H}_6 + 8\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{CO} + 8\text{H}_2\text{O} + \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH}
\]  
(27)

Here, it should be clear that counting atoms does not work and the development of pictures representing the partial oxidation of ethane requires a significant effort. Sankaranarayanan et al.\textsuperscript{6} have studied the catalytic oxidation of ethane based on the following set of pictures

\[
\text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}
\]  
(28a)

\[
\text{C}_2\text{H}_6 + \frac{3}{2}\text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}
\]  
(28b)

\[
\text{C}_2\text{H}_6 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O}
\]  
(28c)

\[
\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O},
\]  
(28d)

and a rigorous method of constructing these types of schemata is described elsewhere (See Appendix C3 of Ref. 3). Rather than become involved in the lengthy analysis needed to develop Eqs. 28, it is much easier to follow the route outlined by Eqs. 13 through 23. We begin this process with a visual representation of the atomic matrix given by

\[
\text{MolecularSpecies} \rightarrow \text{C}_2\text{H}_6 \text{ O}_2 \text{ CO}_2 \text{ H}_2\text{O} \text{ C}_2\text{H}_4 \text{ C}_3\text{H}_5\text{OOH}
\]

\[
\begin{array}{ccccccc}
\text{carbon} & 2 & 0 & 1 & 1 & 0 & 2 \\
\text{hydrogen} & 6 & 0 & 0 & 0 & 2 & 4 \\
\text{oxygen} & 0 & 2 & 2 & 1 & 1 & 0 \\
\end{array}
\]  
(29)

in which C2H6, O2, and CO2 represent the nonpivot species. Use of this form of the atomic matrix in Eq. 13 leads to

\[
\begin{pmatrix}
2 & 0 & 1 & 1 & 0 & 2 \\
6 & 0 & 0 & 0 & 2 & 4 \\
0 & 2 & 2 & 1 & 1 & 0
\end{pmatrix}
\begin{pmatrix}
R_{\text{C}_2\text{H}_6} \\
R_{\text{O}_2} \\
R_{\text{CO}_2} \\
R_{\text{H}_2\text{O}} \\
R_{\text{C}_2\text{H}_4} \\
R_{\text{C}_3\text{H}_5\text{OOH}}
\end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}
\]  
(30)

in which all the atomic species (C, H, and O) are present in at least one nonpivot species. Using several elementary row operations, we can express the atomic matrix in row-reduced echelon form so that Eq. 30 takes the form

\[
\begin{pmatrix}
1 & 0 & 0 & 0 & 1 & 2 & 2 \\
0 & 1 & 0 & 1 & 2 & 1 & 1 \\
0 & 0 & 1 & 1 & 2 & 2 & 2
\end{pmatrix}
\begin{pmatrix}
R_{\text{C}_2\text{H}_6} \\
R_{\text{O}_2} \\
R_{\text{CO}_2} \\
R_{\text{H}_2\text{O}} \\
R_{\text{C}_2\text{H}_4} \\
R_{\text{C}_3\text{H}_5\text{OOH}}
\end{pmatrix}
= \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}
\]  
(31)
Application of the obvious row-column partition leads to

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} R_{C_2H_6} \\ R_{O_2} \\ R_{CO} \end{bmatrix} + \begin{bmatrix} 0 & \frac{1}{3} & \frac{2}{3} \\ \frac{1}{3} & \frac{7}{6} & \frac{2}{3} \\ \frac{1}{2} & \frac{2}{3} & \frac{2}{3} \end{bmatrix} \begin{bmatrix} R_{CO} \\ R_{H_2O} \\ R_{C_2H_4} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}.$$  (32)

and this immediately provides an example of the pivot theorem given by

$$\begin{bmatrix} R_{C_2H_6} \\ R_{O_2} \\ R_{CO} \end{bmatrix} = \begin{bmatrix} 0 & \frac{1}{3} & \frac{2}{3} \\ \frac{1}{3} & \frac{7}{6} & \frac{2}{3} \\ \frac{1}{2} & \frac{2}{3} & \frac{2}{3} \end{bmatrix}^{-1} \begin{bmatrix} R_{CO} \\ R_{H_2O} \\ R_{C_2H_4} \end{bmatrix}.$$  (33)

Equating the elements of the left- and right-hand sides provides the net rates of production of the nonpivot species in terms of the net rates of production of the pivot species.

R_{C_2H_4} = 0 - \frac{1}{3}R_{H_2O} - \frac{2}{3}R_{C_2H_6} - \frac{2}{3}R_{CH_3COOH}  (34a)

R_{O_2} = \frac{1}{2}R_{CO} - \frac{7}{6}R_{H_2O} + \frac{2}{3}R_{C_2H_6} - \frac{1}{3}R_{CH_3COOH}  (34b)

R_{CO} = -R_{CO} + \frac{2}{3}R_{H_2O} - \frac{2}{3}R_{C_2H_4} + \frac{2}{3}R_{CH_3COOH}     (34c)

These three results are consistent with the pictures given by Eqs. 28; however, the development of Eqs. 34 is easier, and the reliability of the result is greater.

**Global Stoichiometry**

Statements concerning the products of a reaction are generally made on the basis of macroscopic observation. Thus, the products associated with the catalytic combustion of ethane are determined by the macroscopic observation of a reactor such as we have illustrated in Figures 1 and 2. In many cases, there may be other species in the product stream that are difficult to detect, and we have suggested this possibility in Figure 3.

If those other species are present in very small amounts, the prediction given by Axiom II will be acceptable. Here, it should be clear that the implementation of Axiom II depends on the judgment that one makes concerning the molecular species that are present in the system.

Up to this point we have discussed the local form of Axiom II, that is, the form that applies at a point in space. However, when Axiom II is used to analyze the reactor shown in Figure 3, we will make use of an integrated form of Eq. 11 that applies to the control volume illustrated in Figure 4. There we have illustrated the local rate of production for species A, designated by \( \mathcal{P}_A \), and the global rate of production for species A, designated by \( \mathcal{P}_A \). The latter is defined by

\[
\mathcal{P}_A = \frac{\partial n_A}{\partial t} = \left\{ \frac{\text{net macroscopic molar rate of production of species A}}{\text{owing to chemical reactions}} \right\}
\]

and we often use an abbreviated description given by

\[
\mathcal{P}_A = \left\{ \frac{\text{global rate of production of species A}}{\text{A = 1, 2, ..., N}} \right\}
\]

When dealing with a problem that involves the global rate of production, we need to form the volume integral of Eq. 11 to obtain

\[
\int_{V}^{A} \sum_{A_{i=1}}^{N} N_{i} \ dV = 0, \quad J = 1, 2, ..., T
\]

The integral can be taken inside the summation operation, and we can make use of the fact that the elements of \( N_A \) are independent of space to obtain

\[
\sum_{A_{i=1}}^{N} N_{i} \int_{V}^{A} \ dV = 0, \quad J = 1, 2, ..., T
\]

Use of the definition of the global rate of production for species A given by Eq. 35 leads to the following global form of Axiom II:

\[
\text{Axiom II (global form):} \quad \sum_{A_{i=1}}^{N} N_{i} \mathcal{P}_A = 0, \quad J = 1, 2, ..., T
\]

**Figure 3. Undetermined products.**

**Figure 4. Local and global rates of production.**
Here, one must remember that $R_A$ has units of moles per unit time while $R_A$ has units of moles per unit time per unit volume, and thus, the physical interpretation of these two quantities is different as illustrated in Figure 4.

The analysis at the macroscopic scale follows that given by Eqs. 13 through 23 and it leads to the pivot theorem for the global rates of production given by

\[ \mathcal{R}_{NP} = \mathcal{P} \cdot \mathcal{R}_P \] (40)

This result is essential for the analysis of macroscopic systems because it specifies the global net rates of production that must be inferred from measurements of the composition, selectivity, conversion, and yield. In Appendix B, we show that there is an equivalent pivot theorem for atomic species balances as opposed to the molecular species balances associated with Eq. 40. For atomic species, this same pivot theorem appears in the transient analysis of batch reactors and the steady-state analysis of continuous stirred tank reactors (CSTR).

\section*{Elementary Stoichiometry}

Knowledge of the global net rates of production indicated by Eq. 35 allows us to analyze reactors from the macroscopic point of view, but it does not allow us to design reactors. For design we need to be able to predict the net rates of production in terms of the concentration of the species involved in the reaction, that is, $C_A, C_B,$ and so forth. To accomplish this, we need to represent the net rates of production, $R_A, R_B, R_C$, and so forth in terms of chemical reaction rates or kinetic models. One approach is to develop models based on a series of elementary rates of production identified as $R_A, R_B, R_C, \ldots, R_M, R_{M+1}, \ldots, R_{M+K}$, and so forth. To illustrate how this is done, we begin with a set of $K$ elementary rates of production that are constrained by elementary stoichiometric conditions given by

\begin{equation}
\sum_{A=1}^{A=M} N_{IA} R^k_A = 0, \quad J = 1, 2, \ldots, T, \quad k = 1, \ldots, K \tag{41}
\end{equation}

Here, we note that there are $M$ species under consideration. The first $N$ of these species are stable molecular species, such as we have illustrated in Figures 1 and 2, whereas species $N + 1$ through $M$ represent the unstable species that are identified in Figure 3 as the "other species." We will refer to these species as "reactive intermediates" or as "Bodenstein products." The sum of the elementary rates of production provide us with the net rate of production as indicated by

\begin{equation}
R_A = \sum_{k=1}^{K} R_k^A, \quad A = 1, 2, \ldots, N, N + 1, \ldots, M \tag{42}
\end{equation}

Associated with each elementary kinetic model, $k = 1, \ldots, K$, one chooses a "reference reaction rate" designated by $r_0, r_1, \ldots, r_K$. These reference reaction rates are used to express the elementary rate of production of species $A$ as

\begin{equation}
R^k_A = M_{AK} r_k, \quad A = 1, 2, \ldots, M, \quad k = 1, \ldots, K \tag{43}
\end{equation}

in which $M_{AK}$ is a component of the mechanistic matrix. This representation of the elementary rate of production can be used with Eq. 42 to express the net rate of production of species $A$ as

\begin{equation}
R_A = \sum_{k=1}^{K} M_{AK} r_k, \quad A = 1, 2, \ldots, N, N + 1, \ldots, M \tag{44}
\end{equation}

In matrix form we express this result as

\begin{equation}
\begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
\vdots \\
R_K \\
R_{N+1} \\
R_M
\end{bmatrix} =
\begin{bmatrix}
M_{11} & M_{12} & M_{13} & \cdots & M_{1K} \\
M_{21} & M_{22} & M_{23} & \cdots & M_{2K} \\
M_{31} & M_{32} & M_{33} & \cdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
M_{N1} & M_{N2} & M_{N3} & \cdots & M_{NK} \\
M_{N+11} & M_{N+12} & M_{N+13} & \cdots & \vdots \\
M_{M1} & M_{M2} & M_{M3} & \cdots & M_{MK}
\end{bmatrix}
\begin{bmatrix}
r_1 \\
r_2 \\
r_3 \\
\vdots \\
r_K \\
r_{N+1} \\
r_M
\end{bmatrix}
\end{equation}

while in compact matrix notation we have

\begin{equation}
R_M = Mr \tag{45}
\end{equation}

Here, $M$ is the mechanistic matrix, $R_M$ is the column matrix of all the net rates of production, and $r$ is the column matrix of reference reaction rates.

The Bodenstein products ($N + 1$ through $M$) are often subjected to the approximation of local reaction equilibrium that is also referred to as the steady-state assumption or the steady-state hypothesis or the pseudo steady-state hypothesis. These are appropriate phrases when kinetic mechanisms are being studied by means of a batch reactor, however, the phrase local reaction equilibrium is preferred because it is not process-dependent. To apply the approximation of local reaction equilibrium, it is convenient to construct a rowflow partition of Eq. 45 as indicated by

\begin{equation}
\begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
\vdots \\
R_K \\
R_{N+1} \\
R_M
\end{bmatrix} =
\begin{bmatrix}
M_{11} & M_{12} & M_{13} & \cdots & M_{1K} \\
M_{21} & M_{22} & M_{23} & \cdots & M_{2K} \\
M_{31} & M_{32} & M_{33} & \cdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
M_{N1} & M_{N2} & M_{N3} & \cdots & M_{NK} \\
M_{N+11} & M_{N+12} & M_{N+13} & \cdots & \vdots \\
M_{M1} & M_{M2} & M_{M3} & \cdots & M_{MK}
\end{bmatrix}
\begin{bmatrix}
r_1 \\
r_2 \\
r_3 \\
\vdots \\
r_K \\
r_{N+1} \\
r_M
\end{bmatrix}
\end{equation}

\begin{equation}
R_M = Mr \tag{47}
\end{equation}
This partition leads to the following two matrix equations

\[
\begin{bmatrix}
R_1 \\
R_2 \\
\vdots \\
R_N
\end{bmatrix} =
\begin{bmatrix}
M_{11} & M_{12} & \cdots & M_{1N} \\
M_{21} & M_{22} & \cdots & M_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
M_{N1} & M_{N2} & \cdots & M_{NN}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
\rho_2 \\
\vdots \\
\rho_N
\end{bmatrix}
\]  
(48a)

\[
\begin{bmatrix}
R_{N+1} \\
R_M
\end{bmatrix} =
\begin{bmatrix}
M_{N+11} & M_{N+12} & \cdots & M_{N+1N} \\
M_{M1} & \cdots & \cdots & M_{MN}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
\rho_2 \\
\vdots \\
\rho_K
\end{bmatrix}
\]  
(48b)

In terms of compact notation, we express the first of these two results as

\[ R = SR \]  
(49)

in which \( R \) is the same column matrix of net rates of production that appears in Eq. 13. We refer to \( S \) as the stoichiometric matrix; however, we must be careful to note that the pivot matrix appearing in Eq. 23 is also composed of stoichiometric coefficients. Because of this, there is a possibility of confusion when referring to “stoichiometric coefficients.” The second of Eqs. 48 can be expressed as

\[ R_B = Br \]  
(50)

in which \( R_B \) is the column matrix of net rates of production for the Bodenstein products, and \( B \) is the Bodenstein matrix. The classic resolution of this set of equations is to impose the condition of local reaction equilibrium expressed as

\[ R_B = 0 \]  
(51)

and use the result from Eq. 50 to eliminate the concentration of the Bodenstein products from the column matrix of reference reaction rates in Eq. 49. In this manner, Eq. 49 becomes a key element in the design of a chemical reactor.

At this point, we are ready to return to Eq. 43 and indicate how one applies elementary stoichiometry in the process of determining the elements of the mechanistic matrix. To accomplish this, we consider the classic example of the reaction of hydrogen with bromine to form hydrogen bromide. The elementary chemical kinetic steps associated with the reaction of \( H_2 \) with \( Br_2 \) to form \( HBr \) are illustrated by:

Elementary chemical kinetic schema I: \( Br_2 \overset{k_1}{\rightarrow} 2Br \)  
(52a)

Elementary chemical kinetic schema II:

\[ Br + H_2 \overset{k_2}{\rightarrow} HBr + H \]  
(52b)

Elementary chemical kinetic schema III:

\[ H + Br_2 \overset{k_3}{\rightarrow} HBr + Br \]  
(52c)

Elementary kinetic schema IV: \( H + HBr \overset{k_4}{\rightarrow} H_2 + Br \)  
(52d)

Elementary kinetic schema V: \( 2Br \overset{k_5}{\rightarrow} Br_2 \)  
(52e)

It is important to note that the schemata listed in Eqs. 52 are not linearly independent. In fact, there is no physical requirement that this be the case, thus, the stoichiometric matrix \( S \) that appears in Eq. 49 may have a rank less than \( N \). This list of schemata represents a set of pictures and what we need for analysis are equations. We indicate how to develop these equations in the following paragraphs.

When the rules of mass action kinetics are applied to the picture given by Eq. 52a, we obtain the following equation

Elementary chemical reaction rate equation I: \( R^i_{Br_2} = -k_1 C_{Br_2} \)  
(53)

and on the basis of this expression, we choose the “reference reaction rate” to be

Elementary reference reaction rate I: \( r_1 \equiv k_1 C_{Br_2} \)  
(54)

Next we need to make use of elementary stoichiometry, thus, we recall Eq. 41 with \( k = 1 \) to obtain

\[ \sum_{h=1}^{A-M} N_{3h} R^h_B = 0, \quad J = Br \]  
(55)

As this process involves only \( Br_2 \) and \( Br \), we see that Eq. 55 provides

\[ 2R^i_{Br_2} + R^l_{Br} = 0 \]  
(56)

and this immediately leads to

Elementary stoichiometry I: \( R^l_{Br_2} = -R^l_{Br} \)  
(57)

This represents a mathematical statement that the atoms of bromine are conserved during the process illustrated by Eq. 52a; however, this result is usually considered to be intuitively obvious and thus is not identified as elementary stoichiometry. One can think of Eq. 57 as an example of “counting atoms” in the same manner that led from the picture given by Eq. 24 to the equation given by Eq. 25. However, we believe that Eq. 57 should be clearly identified as a stoichiometric result based on the application of Eq. 41.

We can summarize the results for the schemata given by Eqs. 52 as follows:

**SCHEMA 1**

Elementary chemical kinetic schema I: \( Br_2 \overset{k_4}{\rightarrow} 2Br \)  
(58a)

Elementary chemical reaction rate equation I: \( R^l_{Br_2} = -k_1 C_{Br_2} \)  
(58b)

Elementary stoichiometry I: \( R^l_{Br_2} = -R^l_{Br} \)  
(58c)
Elementary reference reaction rate I: \[ r_1 = k_1 c_{Br^{-}} \] (58c)
Elementary stoichiometry I: \[ R_{Br}^{1} = -\frac{R_{Br}^{2}}{2} \] (58d)

SCHEMA II

Elementary chemical kinetic schema II:
\[ \text{Br} + H_2 \xrightarrow{k_0} \text{HBr} + H \] (59a)
Elementary chemical reaction rate equation II:
\[ R_{H}^{II} = -k_{II} c_{Br} c_{H_2} \] (59b)
Elementary reference reaction rate II:
\[ r_{II} = k_{II} c_{Br} c_{H_2} \] (59c)
Elementary stoichiometry II: \[ R_{Br}^{II} = R_{H}^{II}; \quad R_{Br}^{II} = -R_{H}^{II} \] (59d)

SCHEMA III

Elementary chemical kinetic schema III:
\[ H + Br_2 \xrightarrow{k_{III}} HBr + Br \] (60a)
Elementary chemical reaction rate equation III:
\[ R_{H}^{III} = -k_{III} c_{H} c_{Br_2} \] (60b)
Elementary reference reaction rate III:
\[ r_{III} = k_{III} c_{H} c_{Br_2} \] (60c)
Elementary stoichiometry III: \[ R_{Br}^{III} = R_{H}^{III}; \quad R_{Br}^{III} = -R_{H}^{III} \] (60d)

SCHEMA IV

Elementary chemical kinetic schema IV:
\[ H + HBr \xrightarrow{k_{IV}} H_2 + Br \] (61a)
Elementary chemical reaction rate equation IV:
\[ R_{H}^{IV} = -k_{IV} c_{H} c_{HBr} \] (61b)
Elementary reference reaction rate IV:
\[ r_{IV} = k_{IV} c_{H} c_{HBr} \] (61c)
Elementary stoichiometry IV: \[ R_{Br}^{IV} = R_{H}^{IV}; \quad R_{Br}^{IV} = -R_{H}^{IV} \] (61d)

SCHEMA V

Elementary chemical kinetic schema V:
\[ 2Br \xrightarrow{k_0} Br_2 \] (62a)
Elementary chemical reaction rate equation V: \[ R_{Br}^{V} = -k_{V} c_{Br}^2 \] (62b)
Elementary reference reaction rate V: \[ r_{V} = k_{V} c_{Br}^2 \] (62c)

Elementary stoichiometry V: \[ \frac{R_{Br}^{V}}{2} = -R_{Br}^{V} \] (62d)

We begin our analysis of Eqs. 58 through 62 by listing the net molar rate of production of all five species in terms of the elementary rates of production according to
\[ R_{Br} = R_{Br}^{I} + R_{Br}^{II} + R_{Br}^{III} + R_{Br}^{IV} + R_{Br}^{V} \] (63a)
\[ R_{H} = R_{H}^{I} + R_{H}^{II} + R_{H}^{III} + R_{H}^{IV} + R_{H}^{V} \] (63b)
\[ R_{HBr} = R_{HBr}^{I} + R_{HBr}^{II} + R_{HBr}^{III} + R_{HBr}^{IV} + R_{HBr}^{V} \] (63c)
\[ R_{IV} = R_{IV}^{I} + R_{IV}^{II} + R_{IV}^{III} + R_{IV}^{IV} + R_{IV}^{V} \] (63d)
\[ R_{Br} = R_{Br}^{I} + R_{Br}^{II} + R_{Br}^{III} + R_{Br}^{IV} + R_{Br}^{V} \] (63e)

At this point, we can use the reference reaction rates that appear in Eqs. 58 through 62 to express the net rates of production as
\[ R_{Br} = -r_1 + 0 - r_{II} + 0 + \frac{1}{2} r_{IV} \] (64a)
\[ R_{H} = 0 - r_{II} + 0 + r_{IV} + 0 \] (64b)
\[ R_{HBr} = 0 + r_{II} + r_{III} - r_{IV} + 0 \] (64c)
\[ R_{IV} = 0 + r_{II} - r_{H} - r_{IV} + 0 \] (64d)
\[ R_{Br} = 2r_1 - r_{II} + r_{III} + r_{IV} - r_{V} \] (64e)

In matrix form, the net rates of production given by Eqs. 64 can be expressed as
\[
\begin{bmatrix}
R_{Br} \\
R_{H} \\
R_{HBr} \\
R_{IV} \\
R_{Br}
\end{bmatrix}
= \begin{bmatrix}
-1 & 0 & -1 & 0 & 1/2 \\
0 & -1 & 0 & 1 \\
0 & 1 & 1 & -1 & 0 \\
0 & 1 & -1 & -1 & 0 \\
2 & -1 & 1 & 1 & -1
\end{bmatrix}
\begin{bmatrix}
r_1 \\
r_{II} \\
r_{III} \\
r_{IV} \\
r_{Br}
\end{bmatrix}
\] (65)

which is just a special case of Eq. 45. The row/row partition illustrated by Eqs. 47 and 48 can be applied to this matrix equation to obtain
\[
\begin{bmatrix}
R_{Br} \\
R_{H} \\
R_{HBr} \\
R_{IV} \\
R_{Br}
\end{bmatrix}
= \begin{bmatrix}
-1 & 0 & -1 & 0 & 1/2 \\
0 & -1 & 0 & 1 \\
0 & 1 & 1 & -1 & 0 \\
0 & 1 & -1 & -1 & 0 \\
2 & -1 & 1 & 1 & -1
\end{bmatrix}
\begin{bmatrix}
r_1 \\
r_{II} \\
r_{III} \\
r_{IV} \\
r_{Br}
\end{bmatrix}
\] (66)

\[
\begin{bmatrix}
R_{Br} \\
R_{H} \\
R_{HBr} \\
R_{IV} \\
R_{Br}
\end{bmatrix}
= \begin{bmatrix}
0 & 1 & -1 & -1 & 0 \\
2 & -1 & 1 & 1 & -1
\end{bmatrix}
\begin{bmatrix}
r_1 \\
r_{II} \\
r_{III} \\
r_{IV} \\
r_{Br}
\end{bmatrix}
\] (67)
At this point, we impose the condition of local reaction equilibrium given by

Local reaction equilibrium: \( R_{\text{H}} = 0, \quad R_{\text{Br}} = 0 \) (68)

This allows us to express Eq. 67 as

\[
\begin{bmatrix}
0 & 1 & -1 & -1 \\
2 & -1 & 1 & 1 & -1
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
\rho_{\text{H}} \\
\rho_{\text{Br}} \\
\rho_{\text{IV}} \\
\rho_{\text{V}}
\end{bmatrix}
= \begin{bmatrix}
0 \\
0
\end{bmatrix}
\]

(69)

and a series of elementary row operations leads to

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & -1/2 \\
0 & 1 & -1 & -1 & 0
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
\rho_{\text{H}} \\
\rho_{\text{Br}} \\
\rho_{\text{IV}} \\
\rho_{\text{V}}
\end{bmatrix}
= \begin{bmatrix}
0 \\
0
\end{bmatrix}
\]

(70)

The reference reaction rates are given in Eq. 58 through Eq. 62, and we summarize those results as

\[
\begin{bmatrix}
\rho_1 \\
\rho_{\text{H}} \\
\rho_{\text{Br}} \\
\rho_{\text{IV}} \\
\rho_{\text{V}}
\end{bmatrix}
= \begin{bmatrix}
\frac{k_1 c_{\text{Br}_2}}{k_{\text{H}2} c_{\text{Br}_2} c_{\text{H}} + k_{\text{IV}2} c_{\text{H}} c_{\text{Br}_2}} \\
\frac{k_{\text{H}2} c_{\text{Br}_2} c_{\text{H}}}{k_{\text{H}2} c_{\text{Br}_2} c_{\text{H}} + k_{\text{IV}2} c_{\text{H}} c_{\text{Br}_2}} \\
\frac{k_{\text{Br}} c_{\text{H}} c_{\text{Br}_2}}{k_{\text{Br}} c_{\text{H}} c_{\text{Br}_2} + k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}} \\
\frac{k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}}{k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2} + k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}} \\
\frac{c_{\text{Br}}}{k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2} + k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}}
\end{bmatrix}
\]

(71)

Use of these representations in Eq. 70 provides

\[
k_1 c_{\text{Br}_2} - \frac{1}{2} k_{\text{IV}} c_{\text{Br}_2} = 0
\]

(72a)

\[
k_{\text{H}2} c_{\text{Br}_2} c_{\text{H}} - k_{\text{Br}} c_{\text{H}} c_{\text{Br}_2} - k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2} = 0
\]

(72b)

and this leads to the following expressions for the concentration of the Bodenstein products:

\[
c_{\text{H}} = \frac{k_{\text{H}2} c_{\text{Br}_2} \sqrt{2k_1 k_{\text{IV}} c_{\text{Br}_2}}}{k_{\text{H}2} c_{\text{Br}_2} + k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}}, \quad c_{\text{Br}} = \sqrt{2k_1 k_{\text{IV}} c_{\text{Br}_2}}
\]

(73)

At this point we make use of Eq. 66 to obtain an expression for the net rate of production of hydrogen bromide that is given by

\[
[R_{\text{BrH}}] = \begin{bmatrix}
0 & 1 & 1 & -1 & 0
\end{bmatrix}
\]

(74)

Next we direct our attention to Eq. 71 and use that result with Eq. 74 to extract the following representation for the net rate of production of hydrogen bromide:

\[
R_{\text{BrH}} = k_{\text{H}2} c_{\text{Br}_2} c_{\text{H}} + k_{\text{Br}} c_{\text{H}} c_{\text{Br}_2} - k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2}
\]

(75)

Finally, we can use the representations for the concentration of \( c_{\text{H}} \) and \( c_{\text{Br}} \) given by Eq. 73 to obtain (after some algebra)

\[
R_{\text{BrH}} = \frac{2k_1 k_{\text{IV}} k_{\text{Br}}}{k_{\text{Br}} + k_{\text{IV}} c_{\text{H}} c_{\text{Br}_2} + c_{\text{H}} k_{\text{Br}} c_{\text{Br}_2}}
\]

(76)

which is exactly the same form as the reaction rate expression determined experimentally by Bodenstein and Lind.\(^\text{12}\) This suggests that the series of kinetic steps illustrated by Eqs. 58 through 62 are consistent with the reaction kinetics; however, one must always remember that the route to Eq. 76 is not necessarily unique. Thus, there may be other schemes that lead to essentially the same result given by Eq. 76.

A key assumption associated with Eq. 76 is that of local reaction equilibrium illustrated in a general sense by Eq. 51 and for this particular case by Eqs. 68. In reality, the net rates of production of the Bodenstein products will never be zero; however, they may be small enough so that Eq. 51 represents an acceptable approximation. For the special case of the hydrogen bromide reaction one can show (See Problem 9-12 of Ref. 3) that small enough means that the following restrictions are satisfied:

\[
R_{\text{Br}} < \frac{2}{3} k_1 c_{\text{Br}_2}/k_{\text{IV}}, \quad R_{\text{H}} < \frac{2}{3} k_1 c_{\text{Br}_2}/k_{\text{IV}}, \quad R_{\text{Br}} < \frac{c_{\text{Br}}}{k_{\text{IV}} c_{\text{Br}} c_{\text{H}}}
\]

(77)

Experimental verification of these restrictions remains as a challenge.

**Conclusions**

In this article, we have examined two applications of stoichiometry. The first of these is the classic situation in which the conservation of \( T \) atomic species is used to constrain the net rates of production of \( N \) molecular species. For single independent reactions, this analysis can be carried out by counting atoms and balancing chemical equations; however, real-world applications rarely involve single independent reactions and matrix methods are required to obtain reliable results. For either local or global stoichiometry, the single application is represented by the pivot matrix that maps the net rates of production of the pivot species onto the net rates of production of nonpivot species. This mapping does not allow one to determine the absolute values of the net rates of production. However, it is essential for the analysis of chemical reactors to determine the experimental values of the net rates of production of the pivot species, \( \rho_{\text{H},1}, \rho_{\text{H},2}, \ldots, \rho_{\text{H},N} \). Two key matrices appeared in this analysis.

The first of these is the atomic matrix that provides for a precise statement of Axiom II, whereas the second is the pivot matrix that maps the net rates of production of the pivot species onto the net rates of production of the nonpivot species. In Appendix B, we show that this same pivot matrix appears in the solution of the atomic species balances for batch reactors and flow-through reactors operating at steady state. For batch reactors, the pivot theorem provides constraints on how the moles of atomic species change during the reaction. For flow-through
reactors operating at steady state, the pivot theorem gives the constraints on the net atomic species molar flow rates that are possible. When charged species (ions) need to be considered, the principle of conservation of charge is easily imposed on the analysis as indicated in Appendix C.

In the study of reaction kinetics, elementary stoichiometry and mass action kinetics are used to develop expressions for all the net rates of production. In this case, the conservation of atomic species is imposed on each elementary step of a set of chemical kinetic steps. These elementary steps are so simple that conservation of atomic species is generally accomplished by "counting atoms"; however, the application of a more rigorous method is described in this article. In this analysis, the mechanistic matrix provides a mapping of reference reaction rates onto all the net rates of production; thus, absolute values of $R_A$, $R_B$, ..., $R_N$ are produced that allow for the design of chemical reactors. When charged species (ions) need to be considered, the principle of conservation of charge is easily imposed on each individual kinetic step as suggested in Appendix C.

Both the pivot matrix and the mechanistic matrix are composed of what are commonly known as stoichiometric coefficients; however, the two sets of stoichiometric coefficients are different, and they serve different functions. Because of this, we need to be precise when we speak about stoichiometry and stoichiometric coefficients.

**Acknowledgments**

This work began many years ago when the authors were challenged by Ruben Carbendi to develop a clear and rational treatment of stoichiometry. Ramon Corro helped the authors meet that challenge, and the authors are grateful for the contributions of these two colleagues. The students who participated in this effort are too numerous to mention, but their contributions are an essential part of this article.

**Notation**

- $A =$ atomic matrix
- $A^T =$ row reduced echelon form of the atomic matrix
- $A_e =$ atomic/electronic matrix
- $c_{RI} =$ interfacial area contained within the volume, $\text{m}^3$
- $B =$ Bodenstein matrix
- $c_i =$ molar concentration of species $A$ (mol/m$^3$)
- $i =$ unit matrix
- $MW_i =$ molecular mass of species $A$ (g/mol)
- $M =$ mechanistic matrix
- $M =$ total number of stable molecular species and Bodenstein products (reactive intermediates)
- $n =$ number of stable molecular species in a multicomponent system
- $N_A =$ number of $J$-type atoms associated with molecular species $A$
- $P =$ pivot matrix
- $R_A =$ net molar rate of production of species $A$ per unit volume (mol/m$^3$)
- $M_R =$ molar rate of production of species $A$ (mol/s)
- $R =$ column matrix of net rates of reaction for stable molecular species (mol/s)
- $R_A =$ column matrix of net rates of production for stable molecular species and Bodenstein products (reactive intermediates) (mol/s)
- $R_N =$ column matrix of net rates of production of the nonpivot species (mol/s)
- $R_P =$ column matrix of net rates of production of the pivot species (mol/s)

**Greek letters**

- $\rho_A =$ mass density of species $A$, kg/m$^3$

**Literature Cited**

Appendix A: Homogeneous and Heterogeneous Reactions

Our analysis of the stoichiometry of heterogeneous reactions is based on conservation of atomic species expressed as

\[ \sum_{A=1}^{A=N} N_{JA} R_A = 0 \]  
(A1)

Here, we adopt the classic continuum point of view and assume that this result is valid everywhere. That is to say that Axiom II is valid in homogeneous regions where \( R_A \) changes slowly and it is valid in interfacial regions where \( R_A \) changes rapidly. We follow the work of Wood et al.\textsuperscript{13} and consider the \( \gamma-\kappa \) interface illustrated in Figure A1.

The volume \( V \) encloses the \( \gamma-\kappa \) interface and extends into the homogeneous regions of both the \( \gamma \)-phase and the \( \kappa \)-phase. The total net rate of production of species \( A \) in the volume \( V \) is represented by

\[ \int_{V} R_A dV = \int_{V_{\gamma}} R_{\kappa A} dV + \int_{V_{\kappa}} R_{\kappa A} dV + \int_{A_{\kappa}} R_{\kappa A} dA \]  
(A2)

Here, the dividing surface that separates the \( \gamma \)-phase from the \( \kappa \)-phase is represented by \( A_{\kappa} \), and the heterogeneous rate of production of species \( A \) is identified by \( R_{\kappa A} \). This quantity is also referred to as the surface excess reaction rate.\textsuperscript{14} Multiplying Eq. A2 by the atomic species indicator and summing over all molecular species leads to

\[ \int_{V} \sum_{A=1}^{A=N} N_{JA} R_A dV = \int_{V_{\gamma}} \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} dV + \int_{V_{\kappa}} \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} dV + \int_{A_{\kappa}} \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} dA, \quad J = 1, 2, \ldots, T \]  
(A3)

From Eq. A1, we see that the left-hand side of this result is zero, and we have

\[ 0 = \int_{V} \sum_{A=1}^{A=N} N_{JA} R_A dV + \int_{V} \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} dV + \int_{V} \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} dA, \quad J = 1, 2, \ldots, T \]  
(A4)

At this point we require that the homogeneous net rates of production satisfy the two constraints given by

\[ \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad J = 1, 2, \ldots, T \]  
(A5)

This leads to the obvious constraint on the heterogeneous rates of production, \( R_{\kappa A} \), and we summarize our results associated with Axiom II as

Axiom II (general) \[ \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad J = 1, 2, \ldots, T \]  
(A6)

Axiom II (homogeneous, \( \gamma \)-phase) \[ \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad J = 1, 2, \ldots, T \]  
(A7)

Axiom II (homogeneous, \( \kappa \)-phase) \[ \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad J = 1, 2, \ldots, T \]  
(A8)

Axiom II (heterogeneous, \( \gamma-\kappa \) interface) \[ \sum_{A=1}^{A=N} N_{JA} R_{\kappa A} = 0, \quad J = 1, 2, \ldots, T \]  
(A9)

These results can be obtained for a more general system (see Ref. 14) in which the \( \gamma-\kappa \) interface represents a moving and deforming surface. For a reactor in which only homogeneous reactions occur (see Figure 1), we make use of Eq. A6 in the form

\[ \text{Axiom II:} \quad AR = 0, \quad R = \begin{bmatrix} R_A \\ R_B \\ \vdots \\ R_N \end{bmatrix} \]  
(A10)

For a catalytic reactor in which only heterogeneous reactions occur at the \( \gamma-\kappa \) interface (see Figure 2), we make use of Eq. A9 in the form

\[ \text{Axiom II:} \quad AR = 0, \quad R = \begin{bmatrix} R_{A1} \\ R_{A2} \\ \vdots \\ R_{AN} \end{bmatrix} \]  
(A11)

Figure A1. Catalytic surface.
The pivot theorem associated with homogeneous reactions is obtained from Eq. A10, and the analysis leads to Eq. 23, which is repeated here as

Pivot Theorem (homogeneous reactions): \( R_M = P R_P \) \( \text{(A12)} \)

The pivot theorem associated with heterogeneous reactions is obtained from Eq. A11 and is given here as

Pivot Theorem (heterogeneous reactions): \( \langle R_A \rangle_{np} = P \langle R_A \rangle_p \) \( \text{(A13)} \)

Here we note that the \textit{axiom} for the conservation of atomic species takes exactly the same form for homogeneous reactions (Eq. A10) and for heterogeneous reactions (Eq. A11). In addition, the \textit{application} of the principle of conservation of atomic species takes exactly the same form for homogeneous reactions (Eq. A12) and for heterogeneous reactions (Eq. A13). The fact that both the \textit{axiom} and the \textit{application} take exactly the same form for homogeneous and heterogeneous reactions has led many to ignore the difference between these two distinct forms of chemical reaction.

In general, measurement of the net rate of production is carried out at the macroscopic level, thus, we normally obtain experimental information for the global net rate of production. For a homogeneous reaction, this takes the form

\[
R_A = \int \frac{R_A \, dA}{\gamma}, \quad A = 1, 2, \ldots, N \quad \text{(A14)}
\]

whereas the global net rate of production for a heterogeneous reaction is given by

\[
R_A = \int \frac{R_A \, dA}{\gamma}, \quad A = 1, 2, \ldots, N \quad \text{(A15)}
\]

Here, we note that the global net rates of production for both homogeneous reactions and heterogeneous reactions have exactly the same physical significance, thus, it is not unreasonable to use the same symbol for both quantities. Given this simplification, the global version of the pivot theorem represented by Eq. 40 applies to both homogeneous and heterogeneous reactions.

**Elementary Stoichiometry and Upscaling**

Moving on to the applications of elementary stoichiometry indicated by Eq. 41, we remark that upsampling of the results from elementary stoichiometry is routine and follows the procedure outlined by Eqs. A14 and A15. However, the key quantity of interest is the representation given by Eq. 46 that we repeat here as

\[
R_M = M \, \bar{r} \quad \text{(A16)}
\]

This result is used in the design of chemical reactors, thus, it is the local volume average form that is needed. In terms of the volume \( \gamma \) indicated in Figure A2, the quantity of interest is \( R_M \), defined by

\[
< R_M > = \frac{1}{\gamma} \int \frac{R_M \, dV}{\gamma} \quad \text{(A17)}
\]

Given that the mechanistic matrix is independent of any upsampling process, we use Eq. A16 to obtain

\[
< R_M > = M \, \bar{r} \quad \text{(A18)}
\]

Here, the simple upsampling results given for Axiom II are lost, and the upsampling process becomes quite complex. For heterogeneous reactions, the reference reaction rates, \( r_i, r_j, r_k, r_m \), and so forth, will depend on surface concentrations, thus surface area averaging of the nonuniform catalytic surface is the first step in the sequence suggested in Figure A2. Given the spatially smooth surface conditions associated with the reference reaction rates, one can upscale those quantities through the hierarchy of length scales indicated in Figure A2 using the method of volume averaging.

**Appendix B: Atomic Species Balances**

The atomic species balance has some advantages when carrying out calculations by hand because the number of atomic species balance equations is almost always less than the number of molecular species balance equations. We begin our development of atomic species balance equations with Axioms I and II given by

**Axiom I:**

\[
\frac{d}{dt} \int \gamma c \, dV + \int \gamma c \cdot n \, dA = \int \gamma R \, dV, \quad A = 1, 2, \ldots, N \quad \text{(B1)}
\]

**Axiom II:**

\[
\sum_{A=1}^{N} \sum_{J=1}^{N} N_{AJ} R_A = 0, \quad J = 1, 2, \ldots, T \quad \text{(B2)}
\]

To develop an atomic species balance, we multiply Eq. B1 by \( N_{AJ} \) and sum over all molecular species to obtain
\[
\sum_{A=1}^{A=N} N_{JA} \int_\Omega c_A d\Omega + \sum_{A=1}^{A=N} N_{JA} \int_\Omega c_A v_A \cdot \mathbf{n} d\Omega = \int_\Omega \sum_{A=1}^{A=N} N_{JA} R_A d\Omega
\]  

(B3)

Here, we have made use of the fact that \( v_A \cdot \mathbf{n} \) is zero everywhere except at the entrances and exits that we have denoted by \( \mathcal{A}_E \). On the basis of Axiom II, we see that the last term in this result is zero, and our atomic species balance takes the form

\[
\sum_{A=1}^{A=N} N_{JA} \frac{d}{dt} \int_\Omega c_A d\Omega + \sum_{A=1}^{A=N} N_{JA} \int_\Omega \nabla c_A \cdot \mathbf{n} d\Omega = 0, \quad J = 1, 2, \ldots, T
\]  

(B4)

in which we have imposed the very reasonable approximation that \( v_A \cdot \mathbf{n} = v \cdot \mathbf{n} \) at the entrances and exits. In Eq. B4, we have indicated explicitly that there are \( T \) atomic species balance equations instead of the \( N \) molecular species balance equations given by Eq. B1. When \( T \leq N \) it may be convenient to solve material balance problems using atomic species balances.

One application of the atomic species balance given by Eq. B4 is based on the total molar concentration of the \( J \)-type atoms that is given by

\[
c_J = \left\{ \sum_{A=1}^{A=N} N_{JA} \right\} = \left\{ \begin{array}{c}
\text{total molar} \\
\text{concentration}
\end{array} \right\}
\quad J = 1, 2, \ldots, T
\]  

(B5)

Use of this result in Eq. B4 leads to the atomic species macroscopic balance given by

Atomic Species Balance: \( \frac{d}{dt} \int_\Omega c_J d\Omega + \int_\Omega c_J \nabla \cdot \mathbf{n} d\Omega = 0, \)  
\( J = 1, 2, \ldots, T \)  

(B6)

This form of the atomic species balance is sometimes useful for solving macroscopic mole balance problems with chemical reactions.

The form represented by Eq. B4 is also useful for the analysis of batch reactors and steady-state reactors such as those illustrated in Figure B1. For the batch reactor, we can express Eq. B4 as

\[
\sum_{A=1}^{A=N} N_{JA} \frac{d n_A}{dt} = 0, \quad J = 1, 2, \ldots, T
\]  

(B7)

in which the total number of moles of species \( A \) in the batch reactor is given explicitly by

\[
n_A = \int_\Omega c_A d\Omega
\]  

(B8)

Integration of Eq. B7 from \( t = 0 \) to \( t = t_f \) yields

\[
\sum_{A=1}^{A=N} N_{JA} \Delta n_A = 0, \quad J = 1, 2, \ldots, T
\]  

(B9)

and in matrix form the first of these becomes

\[
A(\Delta n) = 0
\]  

(B10)

This result is analogous to Eq. 13 and one can follow the analysis from Eq. 13 to Eq. 23 to obtain the pivot theorem for a batch reaction

Pivot Theorem (batch reactor): \( (\Delta n)_{NP} = P(\Delta n)_P \)  

(B11)

Turning our attention to the continuous flow reactor (CSTR) illustrated in Figure B1b, we express the flux term in Eq. B4 as

\[
\int_\Omega c_A \nabla \cdot \mathbf{n} d\Omega = -\int_\Omega c_A \nabla \cdot \mathbf{n} d\Omega + \int_\Omega c_A \nabla \cdot \mathbf{n} d\Omega = \Delta n_A
\]  

(B12)

Use of this expression in the steady-state form of Eq. B4 leads to

\[
\sum_{A=1}^{A=N} N_{JA} \Delta n_A = 0, \quad J = 1, 2, \ldots, T
\]  

(B13)

and in terms of the nomenclature used in Eq. 13, we have

\[
A(\Delta \mathbf{\hat{n}}) = 0
\]  

(B14)

This provides another application of the pivot theorem that we express as

Pivot Theorem (CSTR): \( (\Delta \mathbf{\hat{n}})_{NP} = P(\Delta \mathbf{\hat{n}})_P \)  

(B15)

Both the Eqs. B11 and B15 provide useful tools for the treatment of batch reactors of the type illustrated in Figure B1. The derivation of these results is based on Axiom I and Axiom II along with the uniqueness proof of the row reduced echelon form of the atomic matrix.
Appendix C: Conservation of Charge

The axiom associated with conservation of atomic species was originally stated as

\[
\sum_{A=1}^{A=N} N_{A,J} R_A = 0, \quad J = 1, 2, \ldots, T \tag{C1}
\]

in which \( N \) represents the total number of identifiable stable species such as ethane (C₂H₆), butadiene (C₄H₆), water (H₂O), sulfuric acid (H₂SO₄), and so forth. In addition, if we have a solution of sulfuric acid, the species would include ions such as H⁺ and SO₄²⁻. The matrix form of Eq. C1 is given by

\[
\begin{bmatrix}
N_{11} & N_{12} & N_{13} & \cdots & N_{1,N-1} & N_{1N} \\
N_{21} & N_{22} & N_{23} & \cdots & N_{2,N-1} & N_{2N} \\
\vdots & \vdots & \ddots & \ddots & \vdots & \vdots \\
N_{T1} & N_{T2} & \cdots & N_{T,N-1} & N_{TN}
\end{bmatrix}
\begin{bmatrix}
R_1 \\
R_2 \\
\vdots \\
R_N
\end{bmatrix}
= 0
\tag{C2}
\]

and if some of the species undergoing reaction are charged species (ions), we need to impose conservation of charge in addition to conservation of atomic species. This is done in terms of the additional axiomatic statement given by

\[
\sum_{A=1}^{A=N} N_{eA} R_A = 0 \tag{C3}
\]

in which \( N_{eA} \) represents the electronic charge associated with molecular species \( A \). In terms of matrix representation, Axiom III can be added to Eq. C1 to obtain a combined representation for conservation of atomic species and conservation of charge. This combined representation is given by

\[
\begin{bmatrix}
N_{11} & N_{12} & N_{13} & \cdots & N_{1,N-1} & N_{1N} \\
N_{21} & N_{22} & N_{23} & \cdots & N_{2,N-1} & N_{2N} \\
\vdots & \vdots & \ddots & \ddots & \vdots & \vdots \\
N_{e1} & N_{e2} & \cdots & N_{eN-1} & N_{eN}
\end{bmatrix}
\begin{bmatrix}
R_1 \\
R_2 \\
\vdots \\
R_N
\end{bmatrix}
= 0
\tag{C4}
\]

Here, the elements in the last row of the \((T + 1) \times N\) matrix take on the values associated with the charge on species 1, 2, \ldots, \( N \) as illustrated by

\[
N_{e1} = 0, \quad \text{nonionic species}
\]
\[
N_{e2} = -2, \quad \text{ionic species such as SO}_4^{2-} \tag{C5}
\]
\[
N_{e3} = +1, \quad \text{ionic species such as Na}^+ \tag{C6}
\]

As an example of competing reactions in a redox system, we consider a mixture consisting of ClO₂, H₂O⁺, Cl₂, H₂O, ClO₃⁻, and ClO₂. The visual representation for the atomic/electronic matrix is given by

\[
\begin{bmatrix}
\text{chlorine} & 1 & 0 & 2 & 0 & 1 & 1 \\
\text{oxygen} & 2 & 1 & 0 & 1 & 3 & 2 \\
\text{hydrogen} & 0 & 3 & 0 & 2 & 0 & 0 \\
\text{charge} & -1 & +1 & 0 & 0 & -1 & 0
\end{bmatrix}
\tag{C7}
\]

and use of this result with Eq. C4 leads to

\[
\begin{bmatrix}
1 & 0 & 2 & 0 & 1 & 1 \\
2 & 1 & 0 & 1 & 3 & 2 \\
0 & 3 & 0 & 2 & 0 & 0 \\
-1 & +1 & 0 & 0 & -1 & 0
\end{bmatrix}
= 0
\tag{C8}
\]

At this point, we follow the developments given in this article, and we search for the row reduced echelon form of the atomic/electronic matrix. We begin with

\[
A_e = \begin{bmatrix}
1 & 0 & 2 & 0 & 1 & 1 \\
2 & 1 & 0 & 1 & 3 & 2 \\
0 & 3 & 0 & 2 & 0 & 0 \\
-1 & +1 & 0 & 0 & -1 & 0
\end{bmatrix}
\tag{C9}
\]

and apply a series of elementary row operations to find the row reduced echelon form given by

\[
A_e' = \begin{bmatrix}
1 & 0 & 0 & 0 & 5/3 & 4/3 \\
0 & 1 & 0 & 0 & 2/3 & 4/3 \\
0 & 0 & 1 & 0 & -1/3 & -1/6 \\
0 & 0 & 0 & 1 & -1 & -2
\end{bmatrix}
\tag{C10}
\]

Use of this result in Eq. C7 leads to

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 5/3 & 4/3 \\
0 & 1 & 0 & 0 & 2/3 & 4/3 \\
0 & 0 & 1 & 0 & -1/3 & -1/6 \\
0 & 0 & 0 & 1 & -1 & -2
\end{bmatrix}
\begin{bmatrix}
R_{\text{ClO}_2} \\
R_{\text{H}_2\text{O}^+} \\
R_{\text{Cl}_2} \\
R_{\text{ClO}_3^-} \\
R_{\text{ClO}_2}
\end{bmatrix}
= 0
\tag{C11}
\]
We now follow the type of analysis given in this article, and we apply the obvious column/row partition to obtain

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
R_{\text{ClO}_3}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
+ \begin{bmatrix}
5/3 & 4/3 \\
2/3 & 4/3 \\
-1/3 & -1/6 \\
-1 & -2
\end{bmatrix}
\begin{bmatrix}
R_{\text{ClO}_2}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0 \\
0
\end{bmatrix}
\] (C11)

Making use of the property of the identity matrix leads to

\[
\begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
R_{\text{ClO}_3}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
= \begin{bmatrix}
R_{\text{ClO}_2}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
\] (C12)

and substituting this result in Eq. C11 provides the desired result

\[
\begin{bmatrix}
R_{\text{ClO}_3}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
= \begin{bmatrix}
-5/3 & -4/3 \\
-2/3 & -4/3 \\
1/3 & 1/6 \\
1 & 2
\end{bmatrix}
\begin{bmatrix}
R_{\text{ClO}_2}^\circ \\
R_{\text{H}_2\text{O}^\circ} \\
R_{\text{Cl}^\circ} \\
R_{\text{H}_2\text{O}}
\end{bmatrix}
\] (C13)

Use of Eq. C3 with Eq. C1 is a straightforward matter leading to Eq. C4, and within the framework of local and global stoichiometry, one can apply Eq. C4 in a routine manner to solve problems in which charged species are present. In this case, we see that the net rates of production of the pivot species (ClO$_2^+$ and ClO$_3^-$) must be determined experimentally so that the pivot theorem can be used to determine the net rates of production of the nonpivot species (ClO$_2^-$, H$_2$O$^+$, Cl$_2$, and H$_2$O).

**Mechanistic Matrix**

In our study of reaction kinetics, we made use of chemical reaction rate expressions so that all the net rates of production could be calculated in terms of a series of reference reaction rates. These reference reaction rates were developed on the basis of mass action kinetics and thus contained rate coefficients and the concentrations of the chemical species involved in the reaction. That development made use of elementary stoichiometry, which we express as

Elementary stoichiometry:

\[
\sum_{A=1}^{\Lambda} N_{JA} R_A^k = 0, \quad J = 1, 2, \ldots, T, \quad k = 1, 2, \ldots, K
\] (C14)

This result insures that atomic species are conserved in each elementary kinetic step, and Eq. 11 is satisfied by imposition of the condition

\[
\sum_{\ell=1}^{\nu=K} R_A^\ell = R_A, \quad k = 1, 2, \ldots, K
\] (C15)

When confronted with charged species (ions) in a study of reaction kinetics, one makes use of elementary conservation of charge as indicated by

Elementary conservation of charge:

\[
\sum_{A=1}^{\Lambda} N_{\text{el}} R_A^k = 0, \quad k = 1, 2, \ldots, K
\] (C16)

Thus, charge is conserved in each elementary step of a chemical kinetic schema, and total conservation of charge indicated by Eq. C3 is automatically achieved in the construction of a mechanistic matrix.

*Manuscript received Oct. 4, 2010, revision received Dec. 18, 2010, and final revision received Feb. 9, 2011.*