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A systematic method for reaction invariants and mole balances for complex chemistries

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Abstract

Reaction invariants are quantities that take the same values before, during and after a reaction. We identify a set of reaction invariants that are linear transformations of the species mole numbers. The material balances for chemically reacting mixtures correspond exactly to equating these reaction invariants before and after reaction has taken place. We present a systematic method for determining these reaction invariants from any postulated set of chemical reactions. The strategy presented not only helps in checking the consistency of experimental data, and the reaction chemistry but also greatly simplifies the task of writing material balances for complex reaction chemistries. For examples where the reaction chemistry is not known, we employ Aris and Mah's (Ind. Eng. Chem. Fundam. 2 (1963) 90) classic method to determine a candidate set of chemical equations. Application of reaction invariants in validating proposed reaction chemistry is discussed. One of the important applications of this method is the automation of mole balances in the conceptual design of chemical processes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Conceptual design; Reaction invariants; Mole balances; Complex reactions

Nomenclature

$\boldsymbol{A}$	atomic matrix
$\boldsymbol{A}^*$	echelon form of the atomic matrix obtained by row operations on $\boldsymbol{A}$
$\boldsymbol{B}$	nonsquare matrix of dimension (R, c)
c	total number of reacting and inert components
$\boldsymbol{D}$	square matrix of dimension (R, R)
e	number of elements in the reaction species
$\boldsymbol{F}^0$	column vector of inlet molar flow rates of components
EP_2	economic potential for Level 2 decisions
F_i^0	inlet molar flow rate of component i
F_{lr}^0	inlet molar flow rate of the limiting reactant
$F_{\mathrm{lr}}^{\mathrm{T}}$	total molar flow rate of limiting reactant at the reactor inlet
$\boldsymbol{F}^{\mathrm{T}}$	column vector of total molar flow rates at the reactor inlet
$\boldsymbol{F}_{\mathrm{Ref}}^0$	column vector of the R reference inlet molar flow rates
g	total number of components in the gaseous purge
G	molar flow rate of the gaseous purge stream
$\boldsymbol{I}$	identity matrix of dimension (R, R)
l	total number of components in the liquid purge

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L	molar flow rate of the liquid purge stream
M_i	molar ratio of component i w.r.t. the limiting reactant
$\boldsymbol{M}$	column vector of the molar feed ratios
$\boldsymbol{n}$	column vector of c outlet mole numbers
$\boldsymbol{n}^0$	column vector of the c inlet mole numbers
$\boldsymbol{n}_{\mathrm{Ref}}$	column vector of the outlet mole numbers for the R reference components
$\boldsymbol{n}_{\mathrm{Ref}}^0$	column vector of the inlet mole numbers for the R reference components
n_i	number of moles of component i at the outlet
n_i^0	number of moles of component i at the inlet
N_i	mole number transform of component i
N_i^0	mole number transform of component i based on inlet mole numbers
$\boldsymbol{P}$	column vector of outlet molar flow rates of components
$\boldsymbol{O}$	zero matrix
P_i	outlet molar flow rate of component i
$\boldsymbol{P}_{\mathrm{Ref}}$	column vector of the R reference outlet molar flow rates
R	number of independent reactions
$\mathcal{R}$	rank of the atomic matrix
$\boldsymbol{R}_{\mathrm{g}}$	column vector of flow rates in the gas recycle
$\boldsymbol{R}_{\mathrm{l}}$	column vector of flow rates in the liquid recycle
R_{G}	molar flow rate of gas recycle
R_{L}	molar flow rate of liquid recycle
R_{max}	maximum number of independent reactions
S_i	selectivity to component i
$\mathcal{V}$	nonsquare matrix of dimension (c, R) of stoichiometric coefficients for the c components in the R reactions
$\mathcal{V}_{\mathrm{Ref}}$	square matrix of dimension (R, R) of the stoichiometric coefficients for the R reference components in the R reactions
$\mathcal{V}^{\mathrm{I}}$, $\mathcal{V}^{\mathrm{II}}$	stoichiometric coefficient matrix
$\boldsymbol{x}$	column vector of c mole fractions in the liquid purge stream
$\boldsymbol{x}_{\mathrm{R}}$	column vector of c mole fractions in the liquid recycle stream
x_i	mole fraction of component i in the liquid purge stream
$\boldsymbol{y}$	column vector of c mole fractions in the gaseous purge stream
$\boldsymbol{y}_{\mathrm{R}}$	column vector of c mole fractions in the gaseous recycle stream
y_i	mole fraction of component i in the gaseous purge stream
$\boldsymbol{0}$	column vector of zeroes

Greek letters

α_r	dependence constant for linear combinations
$\boldsymbol{\varepsilon}$	column vector of the R molar extents of reaction
ε_r	molar extent of reaction r
$\nu_{i,r}$	stoichiometric coefficient of component i in reaction r
$\boldsymbol{\nu}_i^{\mathrm{T}}$	row vector of the stoichiometric coefficients for component i in each reaction

Subscripts and superscripts

0	initial
-1	inverse of matrix
i	components
r	reactions
Ref	reference components
T	total

1. Introduction

Three important areas of investigation of a reaction system are, *stoichiometry*, *kinetics* and *mechanism*. Frequently, it is assumed that the stoichiometry of a reaction system is known and, therefore, the main emphasis is laid on determining the mechanism and kinetics. However, getting the stoichiometry correct is equally important and can also be difficult. Smith and Missen (1979) define chemical stoichiometry as the constraints placed on the composition of a closed chemical system by the necessity of conserving the amount of each elemental or atomic species in any physiochemical change of state occurring within the system. Alternatively, Gibbs' rule of stoichiometry must be satisfied by a chemical system (Aris & Mah, 1963). A classic approach for determining the reaction chemistry for a reaction system on the basis of limited experimental observations was published by Aris and Mah (1963). This approach also helps in determining the stoichiometric degrees of freedom. The information needed to implement the method is an accurate knowledge of all the chemical species present in the reaction system. Some of the earliest work in this subject was published by Jouguet (1921) and Defay (1931) (implications of the presence of isomers on the method of Aris and Mah were discussed by Whitwell & Dartt, 1973). This treatment was extended by Happel (1986) to incorporate transient species which may not be observed necessarily in the inlet or outlet of the reaction system. A reaction mechanism involves detailed reactions between reactants, intermediates that may or may not be transient, and the final products in a reaction mixture. The reaction chemistry is determined from a proposed mechanism by eliminating the transient species in the overall scheme. The dependent reactions in the reaction chemistry generated are then eliminated. The mechanistic approach is used widely and is frequently successful. Sometimes, the reaction chemistry generated from a reaction mechanism might contain less than the maximum number of independent reactions. However, Aris and Mah's method always generates a set containing the maximum number of independent reactions. Aris and Mah's approach, therefore, should be considered complimentary to the mechanistic approach. Bonvin and Rippin (1990), and Amrhein, Srinivasan, and Bonvin (1999), used a method called 'Target Factor Analysis' for determination and validation of reaction stoichiometry based on experimentally measured data. Their method is also applicable to systems where the molecular formulae of some of the species is not known.

For a continuous reactor, the number of moles of component i in the outlet can be represented in terms of the inlet moles as

$$n_i = n_i^0 + \boldsymbol{v}_i^{\mathrm{T}} \varepsilon, \quad i = 1, \dots, c, \tag{1}$$

where $\boldsymbol{v}_i^{\mathrm{T}}$ is a row vector of the stoichiometric coefficients of component i in R reactions and $\boldsymbol{\varepsilon}$ is a column vector of the extents of reaction. For simple reaction chemistries where each reaction contains at least one species that is unique only to that reaction, it is easy to write each extent in terms of a single component. For example,

$$n_i = n_i^0 + v_{i1}\varepsilon_1 + v_{i2}\varepsilon_2 + \cdots + v_{i\mathrm{R}}\varepsilon_{\mathrm{R}}, \tag{2}$$

and if component i occurs only in reaction 1, $v_{i2} = v_{i3} = \cdots = v_{i\mathrm{R}} = 0$. Therefore, ε_1 can be expressed solely in terms of moles of i. Similarly, the extent of each reaction can be found, and mole balances can be written by expressing these extents in terms of other components, and eliminating the extents. However, no *systematic* methods are available for writing the material balances for reaction systems of arbitrary complexity where the extent of each reaction cannot be expressed in terms of mole numbers of a single component. Standard textbooks provide a good introduction for developing intuition and skills for writing mole balances (Nauman, 1987; Himmelblau, 1996). Rosen (1962) published an iterative procedure for solving material balances over a reactor, however, the technique had problems with convergence. Sood and Reklaitis (1979), Sood, Reklaitis, and Woods (1979) proposed a procedure which required no iterations for solving material balances for flowsheets. Their procedure, however, needed specification of the extents of reaction for solving balances around a reactor. Schneider and Reklaitis (1975) were among the earliest to consider the relationship between mole balances and element balances for steady-state chemically reacting systems. For simple reaction stoichiometries (e.g. involving one, two or three reactions) it is often possible to write the material balances based on intuition and experience. This task, however, becomes much more difficult for complex reaction chemistries with many reactions. It is, therefore, useful to devise a systematic method to determine the material balances for reaction systems, supposing that the reaction chemistry is known.

To facilitate the numerical treatment of complex reaction systems, many authors have proposed linear and nonlinear transformation of variables (e.g. Waller & Mäkilä, 1981). In their review, Waller and Mäkilä describe various ways to decompose a state vector (consisting of all variables needed to describe the system) into variants and invariants. Denn and Shinnar (1987) used invariants for checking mass balances for coal gasification reactors. These invariants depend on the molar feed ratios to the reactor, but are independent of the type of gasifier used. Reaction invariants are variables that take the same values before, during and after the reaction. They are independent of the extent of reaction, although they may change with flow rate and other parameters. Asbjørnsen and co-workers (Asbjørnsen & Fjeld, 1970; Asbjørnsen, 1972; Fjeld, Asbjørnsen, & Åström, 1974) demonstrated the use of reaction invariants to reduce the dimensionality of the differential equations describing the process dynamics of continuous stirred tank reactors. Srinivasan, Amrhein, and Bonvin (1998) extended this methodology to include flow invariants for such systems. Most of the literature dealing with reaction invariants is related to the process control aspects of a system (Waller & Mäkilä, 1981). Our aim is to employ them for process design. We use linear transformations to determine the reaction invariants which are easy to understand and straightforward to implement. This transformation can be used effectively to go from limited experimental observations to setting up molar balances for a reactor system at steady state. Also, this methodology is useful in planning experiments as it provides an estimate of degrees of freedom necessary for checking data consistency. The use of this systematic methodology in process design applications is demonstrated after the basic method is developed.

2. Reaction invariants

Consider a reaction system consisting of c components undergoing R independent chemical reactions. A block diagram for such a system is shown in Fig. 1. This process block can contain any complex combination of unit operations. The inlet to the process is represented by a c-dimensional column vector of inlet molar flow rate of species, $\mathbf{n}^0$; the outlet of the process is represented by a vector of outlet flow rate of species, $\mathbf{n}$. The R independent chemical reactions are written as

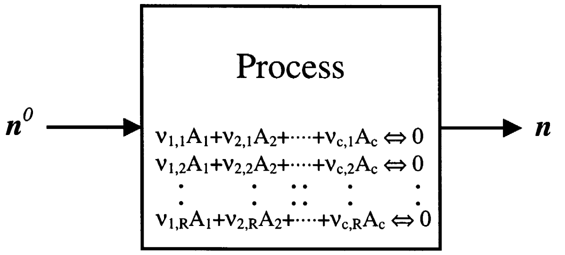

Fig. 1. Block diagram of a reaction system.

$$v_{1,r}A_1 + v_{2,r}A_2 + \cdots + v_{c,r}A_c \rightleftharpoons 0, \quad r = 1,2,\ldots, R, \tag{3}$$

where A_i are the reacting species and $v_{i,r}$ is the stoichiometric coefficient of component i in reaction r. The convention used is $v_{i,r} > 0$ if component i is a product, $v_{i,r} < 0$ if it is a reactant and $v_{i,r} = 0$ if component i is an inert.

In the absence of knowledge about the reactions occurring in the reaction system, it is possible to use Aris and Mah's (1963) method to determine feasible *candidates* for the reaction chemistry based on a knowledge of the species present in the reaction system. This method always gives the maximum number of independent chemical equations for the system. Also, based on the starting point we get a different set of chemical equations. We note, however, that each set of chemical equations can be obtained from any other by linear combinations. The material balances derived from all sets containing the maximum number of independent chemical equations are equivalent (i.e., give the same answers), in spite of the fact that some sets of chemical equations do not correspond to reasonable chemical pathways!

The reaction invariants for the system are given by the transformed mole numbers (Appendix A). Transformed mole numbers take the same value before, during, and after reaction. These are given as

$$N_i^0 = n_i^0 - \mathbf{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}\mathbf{n}_{\mathrm{Ref}}^0, \quad i = 1,\ldots, c - R, \tag{4}$$

$$N_i = n_i - \mathbf{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}\mathbf{n}_{\mathrm{Ref}}, \quad i = 1, \ldots, c - R, \tag{5}$$

where n_i^0 is the number of moles of component i at the inlet, n_i is the number of moles of component i at the outlet, $\mathbf{v}_i^{\mathrm{T}}$ is the row vector of dimension c of the stoichiometric coefficients of component i in all of the R reactions. N_i^0 are the reaction invariants based on the inlet molar flow rates and N_i are the reaction invariants based on the outlet molar flow rates. When we equate these reaction invariants, the mole balances for the reacting system are simply

$$N_i^0 = N_i, \quad i = 1, \ldots, c - R. \tag{6}$$

We note that the number of mole balances for R independent reactions is $c - R$.

The transformed mole numbers represent a linear transformation of the number of moles of species to give conservation relationships which depend only on the reaction chemistry and these linear transformations correspond exactly to the material balances.

3. Properties of mole balances

Property 1. *Mole balances for all sets, each containing the maximum number of independent reactions, are equivalent.*

We consider a reaction chemistry consisting of independent reactions. Using a given set of independent reactions, we can generate a new set by linear combinations. The maximum number of independent reactions is $c-\mathscr{R}$, where $\mathscr{R}$ is the rank of the atomic matrix (Smith & Missen, 1979). The property states that the mole balances for every set with the maximum number of independent chemical equations are equivalent, i.e., they can be obtained from mole balances for any other set with the maximum chemical equations by linear combinations. A proof for this property is given in Appendix B. It also follows from this proof that the mole balances for two sets of chemical equations, each having the same number (but less than the maximum number) of independent reactions, are equivalent if one set of chemical equations can be obtained from the other by linear combinations.

Corollary 1. *Mole balances for two sets of chemical equations are not equivalent if one set cannot be obtained from the other by linear combinations.*

If two sets of chemical equations have the same reaction species and the same number of independent reactions (less than or equal to the maximum number), but if one set cannot be arrived at from the other by linear combinations, the mole balances are not equivalent.

Corollary 2. *Mole balances are equivalent in the presence of dependent chemical equations.*

This means that the mole balances for a given set of independent reactions (a set with maximum or less than maximum number of independent reactions) are equivalent to those for the same set with additional dependent reactions. For example, consider a set of R reactions, out of which $R-1$ are independent. Therefore, the Rth reaction is dependent on the first $(R-1)$ reactions. If ε_r is the extent of the rth reaction, it contributes $v_{i,r}\varepsilon_r$ moles to the total change in the number of moles of the ith species. Therefore, the change in number of moles of the species is given as

$$n_i = n_i^0 + \sum_{r=1}^{R} v_{i,r}\varepsilon_r.$$

Since the Rth reaction is dependent, we can write,

$$v_{i,R} = \sum_{r=1}^{R-1} \alpha_r v_{i,r},$$

where α_r are the dependence constants used for linear combinations. Therefore, we have,

$$n_i - n_i^0 = \sum_{r=1}^{R-1} v_{i,r}\varepsilon_r + v_{i,R}\varepsilon_R \tag{7}$$

$$= \sum_{r=1}^{R-1} v_{i,r}(\varepsilon_r + \alpha_r\varepsilon_R). \tag{8}$$

Redefining $(\varepsilon_r + \alpha_r\varepsilon_R) = \varepsilon_r'$, to be the extent of rth reaction, we have expressed the composition changes in terms of the first $(R-1)$ reactions alone. The procedure in Appendix A eliminates the extents of the reaction, so the mole balances can be determined from the first $R-1$ reactions alone and therefore, give mole balances equivalent to the ones for a set containing only the independent reactions. More details on this can be found in Aris (1965, pp. 14–25).

Property 2. *The mole balances for the maximum number of independent reactions are equivalent to the element balances.*

This means that writing the mole balances for a reaction chemistry using the maximum number of independent reactions is equivalent to writing the balances for conservation of individual elements which constitute the species (e.g. C, H etc.). This property of mole balances and its mathematical proof was published by Schneider and Reklaitis (1975).

Corollary. *Element balances form a subset of the mole balances for less than the maximum number of independent reactions.*

If the reaction chemistry is represented by less than the maximum number of independent reactions, then the element balances are incomplete and form a subset of the mole balances. In such cases, the element balances have more degrees of freedom than the mole balances. A proof of this corollary is given in Appendix C.

4. Categories of mole balances

Case 1. $R = 0$.

For a nonreactive system with c components, the mole balances are given as

$$N_i^0 = N_i, \quad i = 1, \ldots, c. \tag{9}$$

From the definitions of the mole number transforms, the mole balances given in Eq. (9) are equivalent to

$$n_i^0 = n_i, \quad i = 1, \ldots, c. \tag{10}$$

Eq. (10) are the regular mass balances on c components for nonreactive systems.

Case 2. $R = R_{\max}$.

The mole balances for a system with the maximum number of independent reactions is given as

$$N_i^0 = N_i, \quad i = 1, \ldots, \mathscr{R}, \tag{11}$$

where $\mathscr{R}$ is the rank of the atomic matrix (Gadewar, 2001) and $R_{\max} = c - \mathscr{R}$ is the maximum number of independent reactions. Usually, the rank of atomic matrix is same as the number of elements in the reacting species. Therefore, the number of mole balances is equal to the number of elements in such cases. These mole balances are equivalent to the element balances. When the rank of the atomic matrix is less than the number of elements, the *element balances are not independent*. This occurs when every molecule in the system obeys the same fixed stoichiometric relationship(s) between its constituent elements (Appendix D).

Case 3. $R < R_{\max}$.

In the case when the number of reactions is less than the maximum number of independent reactions, the mole balances can be written as

$$N_i^0 = N_i, \quad i = 1, \ldots, \mathscr{R} + r, \tag{12}$$

where $r = R_{\max} - R$. Therefore, there are more mole balances than independent element balances. For such chemistries, element balances give an incomplete view of stoichiometric constraints imposed due to reactions.

Example 1. Hydrodealkylation process.

Let us consider the hydrodealkylation (HDA) of toluene to benzene to elucidate our procedure and exemplify the properties of mole balances. The species present in the reaction system are toluene (C_7H_8), hydrogen (H_2), benzene (C_6H_6), methane (CH_4) and diphenyl ($C_{12}H_{10}$). Although there are many more species present in the process, we only consider the above species in the simplified scheme of reactions given as (Douglas, 1988, p. 126):

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \tag{13a}$$

$$2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2 \tag{13b}$$

We determine the reaction invariants for defining the mole balances by choosing methane and diphenyl as the reference components. The mole balances determined using the method outlined in Appendix A are given as:

$$(n_{C_7H_8} - n^0_{C_7H_8}) + (n_{CH_4} - n^0_{CH_4}) = 0, \tag{14}$$

$$(n_{H_2} - n^0_{H_2}) + (n_{CH_4} - n^0_{CH_4}) - (n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0, \tag{15}$$

$$(n_{C_6H_6} - n^0_{C_6H_6}) - (n_{CH_4} - n^0_{CH_4}) + 2(n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0. \tag{16}$$

These three independent mole balances have ten variables.

The species in the reaction system are numbered as follows: toluene (1), hydrogen (2), benzene (3), methane (4) and diphenyl (5). Using the method of Aris and Mah (1963), we determine a set containing the maximum number of independent reactions. The atomic matrix for this reaction system is given as:

$$\boldsymbol{A} = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccc} (1) & (2) & (3) & (4) & (5) \end{array} \\ \begin{bmatrix} 7 & 0 & 6 & 1 & 12 \\ 8 & 2 & 6 & 4 & 10 \end{bmatrix} \end{array} \tag{17}$$

Here, the columns correspond to the species, and the rows represent the elements. Performing elementary row operations, we reduce the matrix **A** to its echelon form given as:

$$\boldsymbol{A}^* = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccc} (1) & (2) & (3) & (4) & (5) \end{array} \\ \begin{bmatrix} 1 & 0 & \frac{6}{7} & \frac{1}{7} & \frac{12}{7} \\ 0 & 1 & -\frac{3}{7} & \frac{10}{7} & -\frac{13}{7} \end{bmatrix} \end{array} \tag{18}$$

The rank of atomic matrix A is, $\mathscr{R} = 2$. Therefore, the maximum number of independent chemical equations is, $c - \mathscr{R} = 3$. These chemical equations are determined from matrix A^*. Each column in A^* after the unit matrix represents a chemical equation. The chemical equations corresponding to matrix A^* can be determined as follows (Smith & Missen, 1979):

Consider the third column in A^*, the coefficient in the first row of this column is multiplied by the species designated to the first column of the unit matrix. Add this to the coefficient in the second row of the third column multiplied by the species designated to the second column of the unit matrix. This summation is equated to the species designated to the third column giving a chemical equation. Similarly, other chemical equations are written by considering the fourth column and onwards. These chemical equations are given as follows:

$$C_6H_6 \rightleftharpoons \frac{6}{7}C_7H_8 - \frac{3}{7}H_2 \tag{19a}$$

$$CH_4 \rightleftharpoons \frac{1}{7}C_7H_8 + \frac{10}{7}H_2 \tag{19b}$$

$$C_{12}H_{10} \rightleftharpoons \frac{12}{7}C_7H_8 - \frac{13}{7}H_2 \tag{19c}$$

The set of reactions given by Eqs. (19a)–(19c) can be rearranged by linear combinations to give

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \tag{20a}$$

$$2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2 \tag{20b}$$

$$6CH_4 \rightleftharpoons C_6H_6 + 9H_2 \tag{20c}$$

Reactions 20a and 20b are identical to reactions 13a and 13b, while reaction 20c is known to occur on MoO_3 supported on oxides at temperatures above 923 K (Solymosi, Erdohelyi, & Szoke, 1995). Solymosi et al. also found that products like CO_2, H_2O and CO are formed due to the presence of oxygen during the reaction. The process of HDA of toluene (usually given by Eqs. (20a) and (20b)) is conducted catalytically at temperatures of 773–923 K at high pressures over Cr_2O_3, Mo_2O_3 on Al_2O_3 supports (Weissermel & Arpe, 1993, p. 327). Reactions 20a and 20b are also known to be carried out homogeneously at temperatures of 895–978 K (Douglas, 1985). Using our procedure, we determine the mole number transforms for this reaction chemistry. We choose components (3), (4) and (5) as the reference components. Rearranging the mole balances determined using the procedure given in Appendix A, we get

$$7(n_{C_7H_8} - n^0_{C_7H_8}) + 6(n_{C_6H_6} - n^0_{C_6H_6}) + (n_{CH_4} - n^0_{CH_4}) + 12(n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0, \tag{21}$$

$$7(n_{H_2} - n^0_{H_2}) - 3(n_{C_6H_6} - n^0_{C_6H_6}) + 10(n_{CH_4} - n^0_{CH_4}) - 13(n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0. \tag{22}$$

We can write element balances for this system as follows:

Hydrogen balance

$$4(n_{C_7H_8} - n^0_{C_7H_8}) + (n_{H_2} - n^0_{H_2}) + 3(n_{C_6H_6} - n^0_{C_6H_6}) + 2(n_{CH_4} - n^0_{CH_4}) + 5(n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0, \tag{23}$$

Carbon balance

$$7(n_{C_7H_8} - n^0_{C_7H_8}) + 6(n_{C_6H_6} - n^0_{C_6H_6}) + (n_{CH_4} - n^0_{CH_4}) + 12(n_{C_{12}H_{10}} - n^0_{C_{12}H_{10}}) = 0. \tag{24}$$

Eqs. (23) and (24) can be obtained from Eqs. (21) and (22) by linear combinations. Therefore, the mole balances for the maximum number of independent chemical equations are equivalent to the element balances as expected from Property 2. Also, we see that Eqs. (23) and (24) can be obtained from Eqs. (14)–(16) by linear combinations. Note that there are three independent mole balance equations for less than the maximum number of chemical equations (given by Eqs. (14)–(16)) and two independent element balances. The element balances form a subset of the mole balances and, therefore, *element balances are incomplete for chemistries that are represented by less than the maximum number of independent chemical equations* (Corollary to Property 2). This means, for any postulated reaction chemistry with less than the maximum number of independent reactions, element balances need more specifications than mole balances in the estimation of process flow rates usually needed in process design.

5. Applications

5.1. Validating experimental data

Experimental data for reacting mixtures are often described with concentration and flow rate measurements. It is useful to check the measured data for consistency by formulating material balances. The systematic method developed in this paper simplifies and automates the task of setting-up material balances for an experimental reaction system for checking the consistency of measured data.

5.2. Checking proposed reaction chemistry

This is a complement of the previous application. If there is reasonable confidence in the measured data, mole number transforms can be used to determine the molar balances for a proposed reaction chemistry. The agreement of the predictions with the measured data provides validation of the proposed reaction chemistry. We will exemplify this application by considering real examples.

5.3. Complementing experimental data

The degrees of freedom for solving the mole balances determines the minimum number of variables to be measured in order to close the balances. For a reaction system consisting of c components undergoing R reactions, there are $c - R$ independent mole balances and $2c$ variables. Therefore, these balances can be solved by specifying $c + R$ variables. Sometimes it is difficult to measure some species in a reaction system due to adsorption on catalyst, gaseous state, etc., therefore, mole balances help in predicting these values if we can measure $c + R$ variables to close the balances.

5.4. Conceptual design

Heuristic and hierarchical methods are widely used in the chemical process industries (Tyreus & Luyben, 2000). A hierarchical decision procedure for process synthesis was published by Douglas (1985) in which the decisions are decomposed into levels with increasing complexity. We must set-up material balances for evaluating economic tradeoffs, which are used as objectives while proceeding through these decision levels. One of the foremost uses of our mole balance methodology is automating the task of formulating mole balances in Douglas's hierarchical procedure. We will also show this application of our method later in the paper.

Example 2. Dehydrocyclization of propane.

The process of dehydrocyclization of propane is used for upgrading lower alkanes to aromatics which have a higher octane number. Price, Kanazirev, Dooley, and Hart (1998) published an experimental study of this reaction over a cation-containing, proton-poor MFI zeolite catalyst. The gas phase reaction is carried out at 475°C. Measurements for a batch recirculating reactor system give the product distribution at different conversions of propane. However, there is no information in the paper about the reaction chemistry. We therefore use the method of Aris and Mah (1963) to postulate a reaction chemistry and then apply our systematic procedure of mole number transforms to determine the mole balances. Our aim is to setup the mole balances and cross-check the solutions from these mole balances with the experimental observations to determine the consistency of our postulated reaction chemistry.

The reaction species reported in Price et al. (1998) are propane (1), hydrogen (2), methane (3), ethene (4), ethane (5), propene (6), butane (7), butene (8), pentane (9), benzene (10) and toluene (11). Trace amounts of other aromatics are also reported, but we will neglect them in the subsequent analysis. We apply the method of Aris and Mah (1963) to determine a candidate reaction chemistry for this system.The atomic matrix, A, is given as:

$$\boldsymbol{A} = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccccccccc} (1) & (2) & (3) & (4) & (5) & (6) & (7) & (8) & (9) & (10) & (11) \end{array} \\ \left[\begin{array}{ccccccccccc} 3 & 0 & 1 & 2 & 2 & 3 & 4 & 4 & 5 & 6 & 7 \\ 8 & 2 & 4 & 4 & 6 & 6 & 10 & 8 & 12 & 6 & 8 \end{array}\right] \end{array} \tag{25}$$

Here, the columns correspond to the species, and the rows represent the elements present. Performing elementary row operations, we reduce the matrix **A** to its echelon form given as:

$$\boldsymbol{A^*} = \begin{array}{c} \\ C \\ H \end{array} \begin{array}{c} \begin{array}{ccccccccccc} (1) & (2) & (3) & (4) & (5) & (6) & (7) & (8) & (9) & (10) & (11) \end{array} \\ \left[\begin{array}{ccccccccccc} 1 & 0 & \frac{1}{3} & \frac{2}{3} & \frac{2}{3} & 1 & \frac{4}{3} & \frac{4}{3} & \frac{5}{3} & 2 & \frac{7}{3} \\ 0 & 1 & \frac{2}{3} & -\frac{2}{3} & \frac{1}{3} & -1 & -\frac{1}{3} & -\frac{4}{3} & -\frac{2}{3} & -5 & -\frac{16}{3} \end{array}\right] \end{array} \tag{26}$$

The rank of atomic matrix A is, $\mathscr{R} = 2$. Therefore, the maximum number of independent chemical equations is, $c - \mathscr{R} = 9$. These chemical equations are determined from matrix A^*, each column of A^* from the third column onwards yields a chemical equation. The chemical equations corresponding to matrix A^* are given as:

$$CH_4 \rightleftharpoons \frac{1}{3} C_3H_8 + \frac{2}{3} H_2 \tag{27a}$$

$$C_2H_4 \rightleftharpoons \frac{2}{3} C_3H_8 - \frac{2}{3} H_2 \tag{27b}$$

$$C_2H_6 \rightleftharpoons \frac{2}{3} C_3H_8 + \frac{1}{3} H_2 \tag{27c}$$

$$C_3H_6 \rightleftharpoons C_3H_8 - H_2 \tag{27d}$$

$$C_4H_{10} \rightleftharpoons \frac{4}{3} C_3H_8 - \frac{1}{3} H_2 \tag{27e}$$

$$C_4H_8 \rightleftharpoons \frac{4}{3} C_3H_8 - \frac{4}{3} H_2 \tag{27f}$$

$$C_5H_{12} \rightleftharpoons \frac{5}{3} C_3H_8 - \frac{2}{3} H_2 \tag{27g}$$

$$C_6H_6 \rightleftharpoons 2C_3H_8 - 5H_2 \tag{27h}$$

$$C_7H_8 \rightleftharpoons \frac{7}{3} C_3H_8 - \frac{16}{3} H_2 \tag{27i}$$

Rearranging the above equations, we get the following set of chemical equations:

$$C_3H_8 + 2H_2 \rightleftharpoons 3CH_4 \tag{28a}$$

$$2C_3H_8 \rightleftharpoons 3C_2H_4 + 2H_2 \tag{28b}$$

$$2C_3H_8 + H_2 \rightleftharpoons 3C_2H_6 \tag{28c}$$

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \tag{28d}$$

$$4C_3H_8 \rightleftharpoons 3C_4H_{10} + H_2 \tag{28e}$$

$$4C_3H_8 \rightleftharpoons 3C_4H_8 + 4H_2 \tag{28f}$$

$$5C_3H_8 \rightleftharpoons 3C_5H_{12} + 2H_2 \tag{28g}$$

$$2C_3H_8 \rightleftharpoons C_6H_6 + 5H_2 \tag{28h}$$

$$7C_3H_8 \rightleftharpoons 3C_7H_8 + 16H_2 \tag{28i}$$

This set of chemical equations is one among 55 sets that can be determined using the method of Aris and Mah (1963). We know that if we choose any one of these 55 sets, we will get equivalent mole balances (Property 1), so we choose the above set and proceed. Using the procedure outlined in Appendix A, we determine the mole balances for this reaction chemistry. We choose components (1) and (4–11) as the reference components. The mole balances determined using the method outlined in Appendix A and after rearrangements are:

$$\begin{aligned} &3(n_{C_3H_8} - n^0_{C_3H_8}) + (n_{CH_4} - n^0_{CH_4}) + 2(n_{C_2H_4} - n^0_{C_2H_4}) \\ &+ 2(n_{C_2H_6} - n^0_{C_2H_6}) + 3(n_{C_3H_6} - n^0_{C_3H_6}) \\ &+ 4(n_{C_4H_{10}} - n^0_{C_4H_{10}}) + 4(n_{C_4H_8} - n^0_{C_4H_8}) \\ &+ 5(n_{C_{25}H_{12}} - n^0_{C_{25}H_{12}}) + 6(n_{C_6H_6} - n^0_{C_6H_6}) \\ &+ 7(n_{C_7H_8} - n^0_{C_7H_8}) = 0, \end{aligned} \tag{29}$$

$$\begin{aligned} &2(n_{C_3H_8} - n^0_{C_3H_8}) - (n_{H_2} - n^0_{H_2}) + 2(n_{C_2H_4} - n^0_{C_2H_4}) \\ &+ (n_{C_2H_6} - n^0_{C_2H_6}) + 3(n_{C_3H_6} - n^0_{C_3H_6}) \\ &+ 3(n_{C_4H_{10}} - n^0_{C_4H_{10}}) + 4(n_{C_4H_8} - n^0_{C_4H_8}) \\ &+ 4(n_{C_5H_{12}} - n^0_{C_5H_{12}}) + 9(n_{C_6H_6} - n^0_{C_6H_6}) \\ &+ 10(n_{C_7H_8} - n^0_{C_7H_8}) = 0. \end{aligned} \tag{30}$$

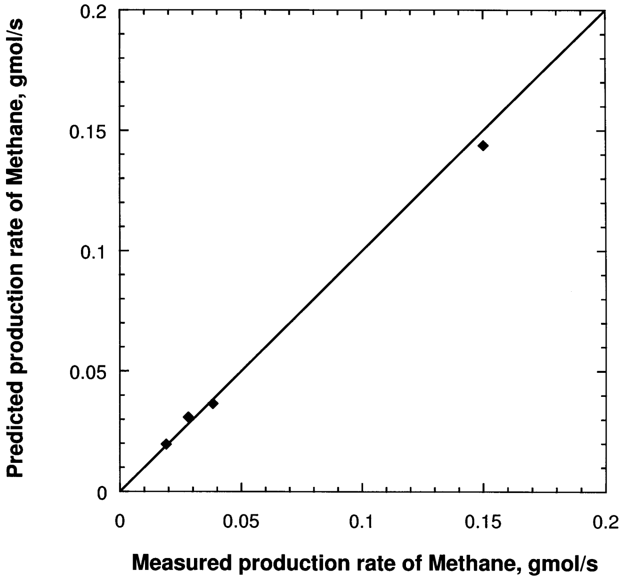

Fig. 2. Parity plot of predicted vs measured production rate of methane.

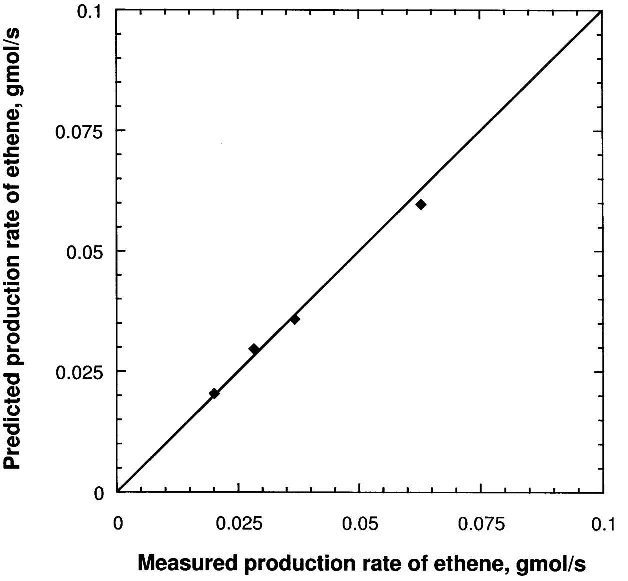

Fig. 3. Parity plot of predicted vs measured production rate of ethene.

Our procedure allows these mole balances to be determined in a completely automated fashion.

5.4.1. Degrees of freedom

The number of variables in the above two equations is 22 ($2c$), and there are 20 ($c+R$) degrees of freedom. The experimental observations from Price et al. (1998, Table 1) are used to specify these 20 degrees of freedom so that we can solve Eqs. (29) and (30). The inlet stream consists only of propane, while the outlet consists of all components. All the outlet flows except hydrogen are measured. Therefore, we have 21 measurements, and hence, one extra measurement to cross-check our predictions.

First, we choose the outlet molar flow rates of methane and hydrogen as unknown variables in the mole balances. Since the outlet flow rate of hydrogen is not measured, we can only cross-check the predicted values of outlet flow rate of methane with the experimentally measured values from Price et al. (1998, Table 1). Fig. 2 shows a parity plot of the predicted vs measured values of methane flow rate at the outlet. Perfect agreement between the predicted values and measured values means that the points lie on the 45-degree line. In Fig. 2, there is a good agreement of our predicted values with the measured values, and the proposed reaction chemistry is consistent with the experimental observations. Now, if we solve the molar balances by choosing outlet flow rates of ethene and hydrogen as unknowns, we can compare the predicted values for ethene with the experimentally measured values from Price et al., Table 1. Fig. 3 again validates the applicability of the proposed reaction chemistry in predicting the dependent molar flow rates.

Example 3. Oxidation of methanol and formaldehyde.

Oxidation of methanol is used industrially to produce formaldehyde which is used primarily as an intermediate in the production of various other chemicals (e.g., Weissermel & Arpe, 1993, p. 35). Cheng (1996) published a study of oxidation of methanol and formaldehyde to study the effect of oxidation of desired product, formaldehyde, into undesired products. The gas phase reaction is carried out at 300°C in the presence of molybdenum oxide catalyst. However, there is no information in the paper about the reaction chemistry. We therefore use the method of Aris and Mah (1963) to propose a set of chemical equations and then apply the systematic procedure of mole balances. Like the last example, our aim is to set up the mole balances and cross-check the solutions from these mole balances with the experimental observations to determine the validity of the proposed reaction chemistry. In this example, however, we will also investigate the effect of using a reaction chemistry with less than the maximum number of chemical equations.

The species present in the reaction system as reported by Cheng (1996) are formaldehyde, methanol, oxygen, nitrogen, water, carbon monoxide, carbon dioxide, dimethyl ether (DME), methyl formate (MF) and methylal (MYL). Nitrogen is an inert in this reaction mixture and we choose to neglect it from subsequent analysis. The system consists of 9 species, comprised of 3 elements. Since the rank of the atomic matrix is 3, the maximum number of independent chemical equations is 6. One such set is given below.

$$CH_3OH+\frac{1}{2}O_2 \rightleftharpoons HCHO+H_2O \tag{31a}$$

$$CH_3OH+CO \rightleftharpoons 2HCHO \tag{31b}$$

$$2HCHO+\frac{1}{2}O_2 \rightleftharpoons CH_3OH+CO_2 \tag{31c}$$

$$CH_3OCH_3+\frac{1}{2}O_2 \rightleftharpoons HCHO+CH_3OH \tag{31d}$$

$$2HCHO \rightleftharpoons HCOOCH_3 \tag{31e}$$

$$C_3H_8O_2+\frac{1}{2}O_2 \rightleftharpoons 2HCHO+CH_3OH \tag{31f}$$

This is one among the 84 possible sets of chemical equations that can be generated using the method of Aris and Mah (1963). The above candidate reaction chemistry might not be the most realistic reaction chemistry for this system, but irrespective of which set we choose, we will arrive at equivalent mole balances (Property 1). Using the formulation developed in Appendix A, we get the following mole balances for the reaction chemistry given by Eqs. (31a)–(31f)

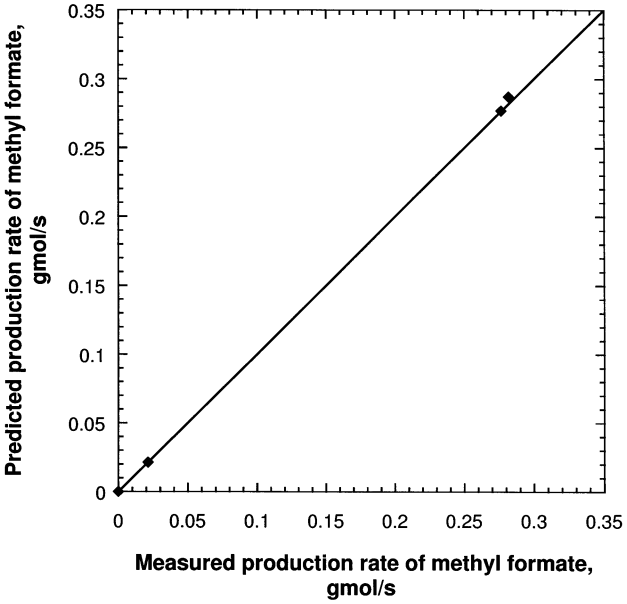

Fig. 4. Parity plot of predicted vs measured production rate of MF.

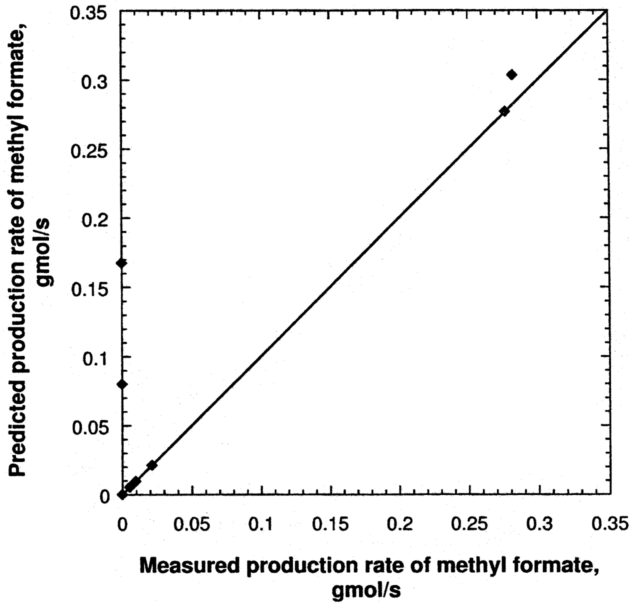

Fig. 5. Parity plot of predicted vs measured production rate of MF neglecting reaction 31d.

$$\begin{aligned}&0.5(n_{CH_3OH}-n^0_{CH_3OH})-(n_{O_2}-n^0_{O_2})-0.5(n_{CO}-n^0_{CO})\\&-(n_{CO_2}-n^0_{CO_2})+(n_{DME}-n^0_{DME})+(n_{MYL}-n^0_{MYL})=0,\end{aligned} \tag{32}$$

$$\begin{aligned}&(n_{CH_3OH}-n^0_{CH_3OH})+(n_{H_2O}-n^0_{H_2O})-(n_{CO}-n^0_{CO})\\&-(n_{CO_2}-n^0_{CO_2})+(n_{DME}-n^0_{DME})+(n_{MYL}-n^0_{MYL})=0,\end{aligned} \tag{33}$$

$$\begin{aligned}&0.5(n_{HCHO}-n^0_{HCHO})+0.5(n_{CH_3OH}-n^0_{CH_3OH})\\&+(n_{MF}-n^0_{MF})+0.5(n_{CO}-n^0_{CO})+0.5(n_{CO_2}-n^0_{CO_2})\\&+(n_{DME}-n^0_{DME})+1.5(n_{MYL}-n^0_{MYL})=0.\end{aligned} \tag{34}$$

We chose formaldehyde, methanol, carbon monoxide, carbon dioxide, DME and MYL as the reference components in getting Eqs. (32)–(34).

5.4.2. Degrees of freedom

The number of variables in Eqs. (32)–(34) is 18 ($2c$), therefore, there are 15 ($c+R$) degrees of freedom. The experimental observations from Cheng (1996, Table 2) are used to specify these 15 degrees of freedom for solving the above mole balances. The inlet consists only of formaldehyde and oxygen while the outlet consists of all the components. There are 16 measurements leaving one variable to be cross-checked with the predictions.

We choose the outlet flow rate of MF as one of the unknowns in the mole balances so we can compare its prediction with the measured values. Fig. 4 shows the parity plot of predicted vs measured production rate of MF. There is a good agreement of the predicted values (determined using the mole balances) with the measured values (Cheng, 1996). Therefore, the proposed reaction chemistry is consistent with the experimental observations. The proposed reaction chemistry consists of six independent reactions, which is the maximum number for the reaction system.

Neglecting any one or more of these reactions may affect the predictions. The mole balances must be determined again for the new set of reactions, which we have done using our procedure. Fig. 5 shows the parity plot of predicted vs measured production rate of MF using mole balances determined after neglecting reaction 31d from the proposed reaction chemistry. There is a significant effect on the accuracy of predictions. Fig. 6 shows the parity plot for the case when reaction 31f is neglected from the set of maximum number of independent reactions. In this case there is little effect on the accuracy of predictions. It should however be noted

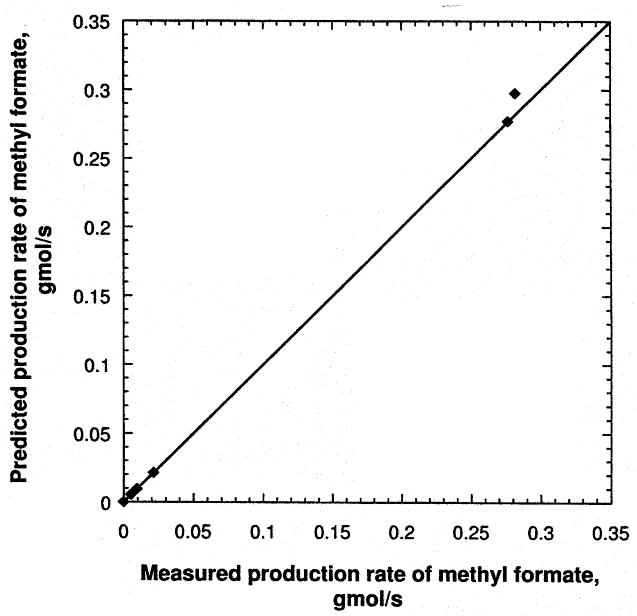

Fig. 6. Parity plot of predicted vs measured production rate of MF neglecting reaction 31f.

that the amount of MYL formed in the experiments as reported by Cheng (1996) is not significant. Therefore, it is not detrimental to neglect reaction 31f in the analysis of the reported experimental data, but reaction 31d cannot be neglected. The methodology developed is not only useful in validating the experimental data, but also in determining the importance of individual chemical reactions in the overall mole balances. Also, if a reaction chemistry is proposed based on intuition and experience (which is done routinely), one can determine if the reaction chemistry is consistent with the experimental observations.

Example 4. Synthesis of 2-methylpyrazine.

Many processes for the production of pharmaceuticals and pesticides are characterized by complex reaction chemistries. Also, biological systems are often represented by complex reaction chemistries. Here, we apply our methodology to a process for the synthesis of 2-methylpyrazine, a pharmaceutical intermediate. Forni and Miglio (1993) performed experiments to study the kinetics of cyclization of ethylenediamine and propylene glycol to 2-methylpyrazine over a Zn–Cr–O/Pd catalyst. The species present in the reaction mixture are reported as ethylenediamine (ED), propylene glycol (PG), 2-methylpyrazine (MP), dihydro-2-methylpyrazine (DHMP), acetone (A), pyrazine (P), dimethylpyrazine (DMP), methanol (M), water, ammonia and hydrogen ($c = 11$). They suggest a mechanism for the reactions in the system and the overall reaction chemistry based on the mechanism is

$$C_2H_8N_2\,(ED) + C_3H_8O_2\,(PG) \rightarrow C_5H_8N_2\,(DHMP) + 2H_2O + 2H_2 \tag{35a}$$

$$C_2H_8N_2\,(ED) + C_3H_8O_2\,(PG) \rightarrow C_5H_6N_2\,(MP) + 2H_2O + 3H_2 \tag{35b}$$

$$C_2H_8N_2\,(ED) + C_3H_8O_2\,(PG) \rightarrow C_4H_4N_2\,(P) + H_2O + 3H_2 + CH_3OH\,(M) \tag{35c}$$

$$C_3H_8O_2\,(PG) \rightarrow C_3H_6O\,(A) + H_2O \tag{35d}$$

$$C_2H_8N_2\,(ED) + C_3H_8O_2\,(PG) \rightarrow 0.5C_6H_8N_2\,(DMP) + 0.5C_4H_4N_2\,(P) + 2H_2O + 3H_2 \tag{35e}$$

$$2C_2H_8N_2\,(ED) \rightarrow C_4H_4N_2\,(P) + 2NH_3 + 3H_2 \tag{35f}$$

The set of reactions 35a–35f has less than the maximum number of independent reactions. The mole balances for the chemical equations 35a–35f are

$$(n_{ED} - n_{ED}^0) - 0.5(n_A - n_A^0) + 0.5(n_M - n_M^0) + 0.5(n_{H_2O} - n_{H_2O}^0) + (n_{NH_3} - n_{NH_3}^0) = 0, \tag{36}$$

$$(n_{PG} - n_{PG}^0) + 0.5(n_A - n_A^0) + 0.5(n_M - n_M^0) + 0.5(n_{H_2O} - n_{H_2O}^0) = 0, \tag{37}$$

$$(n_{MP} - n_{MP}^0) - (n_A - n_A^0) + 2(n_{DMP} - n_{DMP}^0) + 2(n_M - n_M^0) + (n_{H_2O} - n_{H_2O}^0) + 1.5(n_{NH_3} - n_{NH_3}^0) - (n_{H_2} - n_{H_2}^0) = 0, \tag{38}$$

$$(n_{DHMP} - n_{DHMP}^0) + 1.5(n_A - n_A^0) - 1.5(n_M - n_M^0) - 1.5(n_{H_2O} - n_{H_2O}^0) - 1.5(n_{NH_3} - n_{NH_3}^0) + (n_{H_2} - n_{H_2}^0) = 0, \tag{39}$$

$$(n_P - n_P^0) - (n_{DMP} - n_{DMP}^0) - (n_M - n_M^0) - 0.5(n_{NH_3} - n_{NH_3}^0) = 0. \tag{40}$$

We chose acetone, dimethylpyrazine, methanol, water, ammonia and hydrogen as the reference components in the procedure for setting the mole balances.

5.4.3. Degrees of freedom

The number of variables in Eqs. (36)–(40) is 22 ($2c$), therefore, there are 17 ($c + R$) degrees of freedom. If the inlet flow rates for the reaction system are known, the new degrees of freedom are 6 (R). In an experimental protocol, therefore, six product flow rates have to be measured to close the mole balances. More than six product flow rates must be measured for data consistency checks. Therefore, the mole balance methodology provides vital input for planning experiments.

6. Application to conceptual design

The aim of conceptual design is to find the best few candidate process flowsheet(s) and to estimate optimum operating conditions for a given reaction chemistry and production rate(s). Douglas (1985), Douglas (1988, p. 117) proposed a hierarchical approach for conceptual designs. This procedure needs the specification of the streams entering and leaving the process units. The concept of reaction invariants can be applied to simplify the task of identifying the degrees of freedom and the molar balances needed in the hierarchical decision procedure for process synthesis of systems with multiple chemical reactions. The hierarchy of decisions is given as (Douglas, 1985, 1988, 1995)

- Level 0: input data
- Level 1: number of plants
- Level 2: input/output structure and plant connections
- Level 3: recycle structure of the flow sheet and reactor considerations
- Level 4: general structure of the separation system-phase splits
  - ○ Level 4a: vapor recovery system
  - ○ Level 4b: solid recovery system
  - ○ Level 4c: liquid recovery system
  - ○ Level 4d: combine separation system for multiple plants
- Level 5: energy integration
- Level 6: evaluate process alternatives
- Level 7: control system synthesis
- Level 8: hazops analysis

7. Level 2: input–output structure of the flow sheet

A block flow sheet for a typical chemical process is shown in Fig. 7. The process inlet, given by $\boldsymbol{F}^0$, is a vector of fresh feed flow rates into the process while the vector of product and byproduct flow rates is given by $\boldsymbol{P}$. The components in the process may be removed in the purge streams; G, denoting the gaseous purge stream, and L representing the flow rate of liquid purge stream. The overall material balances at Level 2 can be written using the transformed mole numbers as

$$P_i + Gy_i + Lx_i - \boldsymbol{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}(\boldsymbol{P}_{\mathrm{Ref}} + G\boldsymbol{y}_{\mathrm{Ref}} + L\boldsymbol{x}_{\mathrm{Ref}})$$
$$= F_i^0 - \boldsymbol{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}\boldsymbol{F}_{\mathrm{Ref}}^0, \quad i = 1, \ldots, c - R. \tag{41}$$

Here, x_i and y_i are mole fractions of component i in the gas and liquid purge stream, respectively. Accumulation of trace components in a recycle loop can make a process inoperable, purge streams can be used to avoid this accumulation. Joshi and Douglas (1992) published a systematic procedure for identifying exit points in a flowsheet for the removal of trace components. Our analysis relies on the assumption that all the species in the reaction system are known. If some compounds are formed in small amounts by reactions not accounted for, their accumulation may cause problems in operability. Therefore, provisions for their removal in the purge streams must be made. The molar outlet flow of each component is given as the sum of its amount in the product and purge streams. The dimension of each reference vector is R, which is the number of independent reactions.

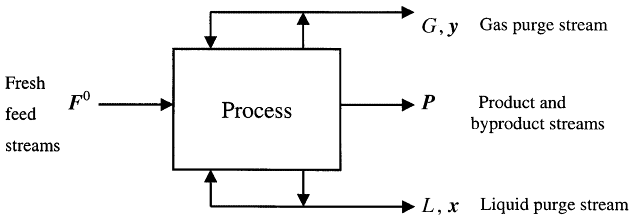

Fig. 7. Block diagram for Level 2 of hierarchical procedure for conceptual design.

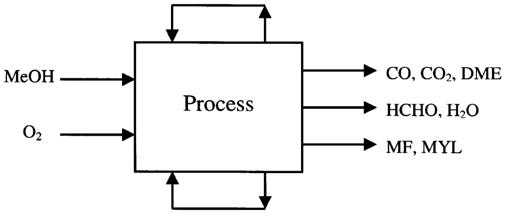

Fig. 8. Block flow sheet for production of formaldehyde from methanol.

7.1. Degrees of freedom

If the number of components in the gaseous and liquid purge is g and l, respectively, the total number of unknowns for a Level 2 balance is $2c + l + g$. These consist of $2c$ variables for fresh feed input streams, and product streams, $(l - 1)$ independent mole fractions in the liquid purge, $(g - 1)$ independent mole fractions in the gas purge, liquid purge flow rate and gas purge flow rate. There are $c - R$ molar balances among these variables. Therefore,

$$\mathrm{DOF} = c + g + l + R. \tag{42}$$

In order to solve the Level 2 balances, it is necessary to specify $c + g + l + R$ variables.

8. Level 2 balances for Example 3

We consider the oxidation of methanol and formaldehyde discussed in Example 3 to demonstrate the application of our method for evaluation of the economic potential at Level 2 (Douglas, 1985). Methanol is the limiting reactant in the process of manufacturing formaldehyde. We assume that there are no liquid or gas purges (i.e., there is a complete recovery of all the reactants). Fig. 8 shows the Level 2 block flow sheet for the process. We use the product distribution vs conver-

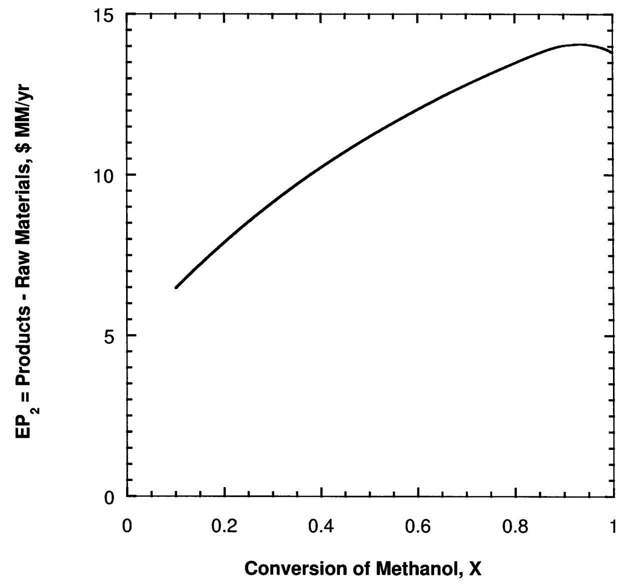

Fig. 9. Economic potential at Level 2 vs conversion of methanol.

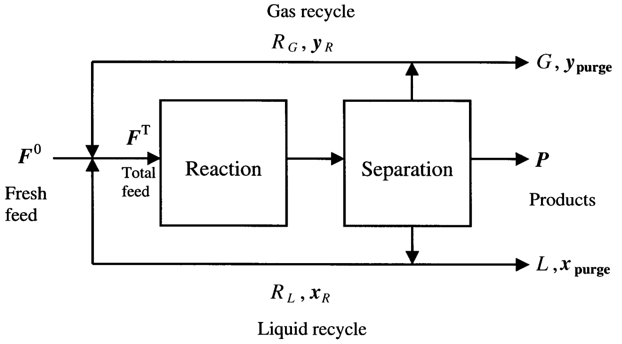

Fig. 10. Block diagram for Level 3 of hierarchical procedure for conceptual design.

sion data reported in Cheng (1996, Fig. 4). The product distribution is reported in terms of the selectivity to the main product, formaldehyde, and the byproducts. We reformulate the mole balances given by Eqs. (32)–(34) in terms of selectivities. The Level 2 balances are given as follows:

$$F^0_{O_2}\frac{S_{HCHO}}{P_{HCHO}} - 0.5S_{CO} - S_{CO_2} + P_{DME}\frac{S_{HCHO}}{P_{HCHO}} + S_{MYL} = 0, \qquad (43)$$

$$P_{H_2O}\frac{S_{HCHO}}{P_{HCHO}} - S_{CO} - S_{CO_2} + P_{DME}\frac{S_{HCHO}}{P_{HCHO}} + S_{MYL} = 1, \qquad (44)$$

$$P_{DME}\frac{S_{HCHO}}{P_{HCHO}} + 0.5S_{CO} + 0.5S_{CO_2} + 0.5S_{HCHO} + S_{MF} + 1.5S_{MYL} = 0.5, \qquad (45)$$

where S_i represents the selectivity defined as the moles of component i produced per mole of limiting reactant consumed. There are $c + R$ degrees of freedom for the material balances on the process block shown in Fig. 8. At Level 2, we specify that there are no reactants in the outlet streams and no products in the inlet streams. These correspond to c specifications. The remaining R degrees of freedom are normally fixed by specifying the production rate of the primary product together with $R - 1$ selectivities. For this example, these correspond to P_{HCHO}, S_{HCHO}, S_{CO}, S_{CO_2}, S_{MYL} and S_{MF}. Eqs. (43)–(45) are then solved for $F^0_{O_2}$, P_{DME} and P_{H_2O}.

Experiments need to be carried out to determine the product distribution (i.e., the $R - 1$ selectivities) at different conversions of the limiting reactant at specified values of the experimental parameters (e.g., reactor configuration, molar feed ratios, pressure, temperature etc.). These are usually decided by the chemist, perhaps in collaboration with an engineer. The selectivities to products and byproducts can then be established either as discrete data points or a selectivity relationship as a function of the experimental parameters. One useful source for getting such information is the "Attainable Region", which is a collection of all the product and byproduct compositions (or selectivities) that can be achieved by using reaction and mixing in all possible combinations (Glasser, Hildebrandt, & Crowe, 1987; Feinberg, 2000).

Many processes for making commodity monomers, specialty polymers and specialty chemicals, pesticides etc., need large number of reaction steps and sometimes separations are required between reactors. Similar characteristics are observed in integrated plant complexes for producing petrochemicals. Douglas (1990) extended the hierarchical procedure for conceptual design to plant complexes. Our methodology for Level 2 balances can also be used for plant complexes.

8.1. Economic potential at Level 2

Single plants for the manufacture of formaldehyde have a capacity of up to 200000 t year^{-1} (Weissermel & Arpe, 1993). We assume that the plant capacity, $P_{HCHO} = 100000$ t year^{-1} for estimating the economic potential. The remaining degrees of freedom are specified using the product distribution given in Cheng (1996, Fig. 4). Eqs. (43)–(45) are solved in conjunction with the definitions of selectivities in terms of component flows enabling the estimation of all the unknown flow rates. The economic potential at Level 2, EP_2, is defined as

$$EP_2 = \text{(Value of formaldehyde)} - \text{(Cost of methanol and oxygen)}. \qquad (46)$$

The plot of EP_2 vs conversion of methanol is shown in Fig. 9. Here, we have assumed that there is no value of the byproducts and we also do not consider the cost of waste treatment. The graph shows that the economic potential increases with conversion before decreasing slightly at very high conversions (> 0.95).

9. Level 3: recycle structure of the flow sheet

A simplified process flow sheet is shown in Fig. 10. The flow sheet consists of a reaction system and a separation system. The determination of recycle flows is critical in evaluating the economic potential for the process. Also, it is necessary for reactor design since the unreacted feed is recycled back to the reactor. Comparing Fig. 7 and Fig. 10, we find that the overall molar balances for Level 3 are the same as for Level 2 since the inlet and outlet streams are identical in both cases. However, at this stage, based on process requirements (often determined by reaction constraints or optimization), some new design variables are often imposed on the process which may include specifying values for molar feed ratios at reactor inlet, equality of composition of the recycle stream and purge stream for gaseous components in the absence of a gas recovery system in the separation block of the flow sheet, etc. This will lead to specification of new variables which were not specified at the Level 2 balances. Depending on the overall degrees of freedom at Level 3, this may result in cancellation of some of the specifications made at Level 2. This happens when

$$\text{(Number of restrictions at Level 3)} > \text{(DOF at Level 3} - \text{DOF at Level 2).} \tag{47}$$

For example, this occurs when the selectivities (used at Level 2) depend on the molar feed ratios at the reactor inlet.

9.1. Degrees of freedom

9.1.1. Case 1

If the mole fractions of the components in the purge streams are the same as the corresponding recycle stream, $\boldsymbol{x}_R$ is the same as $\boldsymbol{x}_{\text{purge}}$ and $\boldsymbol{y}_R$ is the same as $\boldsymbol{y}_{\text{purge}}$ in Fig. 10. Therefore, there are two new variables introduced at this level compared to Level 2, which are the recycle flow rates of the liquid and gaseous streams, respectively. Therefore,

$$\text{DOF} = c + l + g + R + 2.$$

However, since $c + g + l + R$ variables are already specified at Level 2, we must specify two additional degrees of freedom to solve the Level 3 balances. Usually, molar feed ratios at the reactor inlet are chosen. Also, conversion of the limiting reactant is an important variable which is known before solving these balances. In order to incorporate this information, we formulate the recycle balances in terms of molar ratios. However, since the degrees of freedom are unchanged by this new formulation, we may no longer have control over some variables we specified at Level 2 (like purge liquid and gas compositions), which can then be calculated once the recycle balances are solved. This will occur if the condition given in Eq. (47) is satisfied.

The recycle flow rate of the limiting reactant can be written in terms of the feed flow rates by a material balance around the mixing point

$$R_{\text{lr}} = F_{\text{lr}}^{\text{T}} - F_{\text{lr}}^{0}, \tag{48}$$

where F_{lr}^{T} is the total molar flow rate of the limiting reactant at the reactor inlet and F_{lr}^{0} is the fresh molar feed rate of the limiting reactant. The recycle flow rates for all the components can be written as

$$\boldsymbol{R}_{\text{l}} + \boldsymbol{R}_{\text{g}} = \frac{F_{\text{lr}}^{0}}{X_{\text{lr}}} \cdot \boldsymbol{M} - \boldsymbol{F}^{0}. \tag{49}$$

Here, $\boldsymbol{R}_{\text{l}}$ and $\boldsymbol{R}_{\text{g}}$ are the column vectors of the recycle flow rates of c components in the liquid and gas recycle, respectively, X_{lr} is the conversion of the limiting reactant, $\boldsymbol{M}$ is a column vector of the molar feed ratio of components to the limiting reactant at the reactor inlet, where $M_i = F_i^{\text{T}}/F_{\text{lr}}^{\text{T}}$ is the molar feed ratio of component i with respect to the limiting reactant, and $\boldsymbol{F}^{0}$ is the column vector of the fresh molar feed rates of c components. The molar feed ratios at the reactor inlet are usually kept constant during operation to avoid disturbances in the process conditions. Since there are l components in the liquid recycle, $c - l$ values in the column vector $\boldsymbol{R}_{\text{l}}$ are known to be zero. Similarly, $c - g$ values in the column vector $\boldsymbol{R}_{\text{g}}$ are known to be zero. Therefore, we have introduced $c + l + g + 1$ new variables which include c molar ratios, $l + g$ recycle flow rates, and conversion of the limiting reactant. We have $c + 1$ additional equations at Level 3, c equations given in Eq. 49 and $F_{\text{lr}}^{\text{T}} X_{\text{lr}} = F_{\text{lr}}^{0}$. The variables that we specified earlier but need not be specified in the new formulation at Level 3 are $l - 1$ mole fractions in the liquid purge and $g - 1$ mole fractions in the gaseous purge.

9.1.2. Case 2

If a separation system is used to separate the purge stream from the recycle stream, the component mole fractions in the recycle stream will be different from the corresponding purge stream. Therefore, $\boldsymbol{x}_R$ is different from $\boldsymbol{x}_{\text{purge}}$ and $\boldsymbol{y}_R$ is different from $\boldsymbol{y}_{\text{purge}}$ in Fig. 10. If the number of components in the gas and liquid purge streams is g and l, respectively, there are $l + g$ new variables at Level 3 as compared to Level 2. These $l + g$ new variables consist of $(l - 1)$ independent mole fractions in the liquid recycle stream, $(g - 1)$ independent mole fractions in the gas recycle stream, recycle flow rate of liquid and recycle flow rate of gas, given as R_{L} and R_{G}, respectively, in Fig. 10. Therefore,

$\mathrm{DOF} = c + 2l + 2g + R.$

However, since $c + g + l + R$ variables are already specified at Level 2, we must specify $l + g$ additional degrees of freedom to solve the Level 3 balances. The balances given in Eq. (49) along with the Level 2 balances can be solved in this case if the molar feed ratios of components at the reactor inlet are known.

10. Conclusions

We have developed a systematic treatment of input-output mole balances for complex chemistries by using the concept of reaction invariants to determine mole balances for a complex reaction system. If the reaction chemistry is not known, we employ a systematic method by Aris and Mah (1963) to determine a consistent set of chemical equations. We demonstrate the applicability of this method in data reconciliation for two examples, viz., propane dehydrogenation, and oxidation of formaldehyde and methanol. We prove that the mole balances for the maximum number of independent reactions are in fact the element balances and these balances are equivalent for any set of maximum number of independent chemical equations. This methodology also gives the degrees of freedom for experimental analysis of a reaction system and thus provides insight for planning experiments. One of the foremost applications of reaction invariants is in the automation of the hierarchical decision procedure for process synthesis published by Douglas (1985, 1988). This systematic methodology greatly simplifies the task of setting mole balances for complex chemistries at Levels 2 and 3 of Douglas's hierarchical procedure.

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Appendix A. Mole number transforms

Consider a reaction system with a total of c components undergoing R independent chemical reactions. The R independent chemical reactions can be written as:

$$v_{1,r}A_1 + v_{2,r}A_2 + \cdots + v_{c,r}A_c \rightleftharpoons 0, \quad r = 1, 2, \ldots, R. \tag{A.1}$$

Here A_i is the reacting species and $v_{i,r}$ is the stoichiometric coefficient of component i in reaction r. The convention used is $v_{i,r} > 0$ if component i is a product, $v_{i,r} < 0$ if component i is a reactant and $v_{i,r} = 0$ if component i is an inert.

Intuitively, one might think that c molar balances can be written for a reaction system with c components. However, we should take into consideration the constraints imposed by R independent reactions. These constraints can be deployed by using 'extent of reaction' in relating the molar quantities of components. An extent of reaction for reaction r can be defined as:

$$\varepsilon_r = \frac{(n_i - n_i^0)_r}{v_{i,r}}, \tag{A.2}$$

where ε_r is the extent of reaction r, $(n_i - n_i^0)_r$ is the number of moles of component i reacted in reaction r and $v_{i,r}$ is the stoichiometric coefficient of component i in reaction r.

Since a component can be present in more than one reaction, we express the overall consumption (production) of reactants (products) in terms of the 'extents of reaction' as

$$n_i = n_i^0 + \boldsymbol{v}_i^{\mathrm{T}}\boldsymbol{\varepsilon}, \quad i = 1, \ldots, c, \tag{A.3}$$

where n_i^0 is the initial number of moles of component i, n_i is the number of moles of component i at any given time t, $\boldsymbol{v}_i^{\mathrm{T}}$ is the row vector of dimension R of the stoichiometric coefficients of component i in each of the R reactions:

$$\boldsymbol{v}_i^{\mathrm{T}} = (v_{i,1}, \ldots, v_{i,R}) \tag{A.4}$$

and $\boldsymbol{\varepsilon}$ is the column vector of the R extents of reaction for each of the R reactions:

$$\boldsymbol{\varepsilon} = (\varepsilon_1, \ldots, \varepsilon_R)^{\mathrm{T}}. \tag{A.5}$$

Eq. (A.3) can be written as

$$\boldsymbol{n} = \boldsymbol{n}^0 + \mathscr{V}\boldsymbol{\varepsilon} \tag{A.6}$$

with,

$$\mathscr{V} = \begin{bmatrix} v_{1,1} & \cdots & v_{1,R} \\ \vdots & v_{i,r} & \vdots \\ v_{c,1} & \cdots & v_{c,R} \end{bmatrix}$$

is a nonsquare matrix of dimension (c, R) of the stoichiometric coefficients for the c components in the R reactions, and $\boldsymbol{n} = (n_1,\ldots,n_c)^{\mathrm{T}}$ is the column vector of dimension c of mole numbers and $\boldsymbol{n}^0 = (n_1^0,\ldots,n_c^0)^{\mathrm{T}}$ is the column vector of dimension c of the initial mole numbers.

We can eliminate the R extents of reaction from the c equations given by A.6. This can be accomplished by choosing a subsystem of R equations from among the c Eq. (A.6). These are the *reference components* and the reference equations are given as

$$\boldsymbol{n}_{\mathrm{Ref}} = \boldsymbol{n}^0_{\mathrm{Ref}} + \mathcal{V}_{\mathrm{Ref}}\boldsymbol{\varepsilon}. \tag{A.7}$$

Here,

$$\mathcal{V}_{\mathrm{Ref}} = \begin{bmatrix} v_{(c-R+1),i} & \cdots & v_{(c-R+1),R} \\ \vdots & v_{i,r} & \vdots \\ v_{c,1} & \cdots & v_{c,R} \end{bmatrix} \tag{A.8}$$

and $\boldsymbol{n}_{\mathrm{Ref}} = (n_{(c-R+1)},\ldots,n_c)^{\mathrm{T}}$ is the column vector of dimension R of mole numbers for reference components, $\boldsymbol{n}^0_{\mathrm{Ref}} = (n^0_{(c-R+1)},\ldots,n^0_c)^{\mathrm{T}}$ is the column vector of dimension R of the initial mole numbers for the reference components. For convenience, the components are numbered such that the reference components are at the end of the column vector of mole numbers. The reference components should be chosen such that the square matrix $\mathcal{V}_{\mathrm{Ref}}$ is invertible.

Using Eqs. (A.7) and (A.8), the extents of reaction can be expressed as

$$\boldsymbol{\varepsilon} = (\mathcal{V}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}_{\mathrm{Ref}} - \boldsymbol{n}^0_{\mathrm{Ref}}). \tag{A.9}$$

Substituting relation A.9 in Eq. (A.3), we get,

$$n_i = n_i^0 + \boldsymbol{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}_{\mathrm{Ref}} - \boldsymbol{n}^0_{\mathrm{Ref}}), \quad i = 1, \ldots, c-R. \tag{A.10}$$

We now define the 'transformed mole numbers' as:

$$N_i = n_i - \boldsymbol{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}\boldsymbol{n}_{\mathrm{Ref}},$$

$$N_i^0 = n_i^0 - \boldsymbol{v}_i^{\mathrm{T}}(\mathcal{V}_{\mathrm{Ref}})^{-1}\boldsymbol{n}^0_{\mathrm{Ref}}.$$

These quantities allow us to write the mole balances in Eq. (A.10) in the compact form

$$N_i = N_i^0, \quad i = 1, \ldots, c-R. \tag{A.11}$$

We can define $c-R$ transforms and there are $c-R$ mole balances for a system with R independent reactions. Eq. (A.11) says "transformed number of moles in" = "transformed number of moles out", like a mole balance for nonreactive mixtures. These transformed mole numbers also form a basis for transformed compositions used in applying the lever rule for reacting systems (Ung & Doherty, 1995a,b).

Appendix B. Proof of Property 1

Property 1. *Mole balances for all sets, each containing the maximum number of independent reactions, are equivalent.*

Proof 1. Consider a stoichiometric coefficient matrix $\mathcal{V}^{\mathrm{I}}$ which represents a set containing the maximum number of independent reactions. Let $\mathcal{V}^{\mathrm{II}}$ represent another set with the same number of independent reactions. We can get $\mathcal{V}^{\mathrm{II}}$ from $\mathcal{V}^{\mathrm{I}}$ by elementary column operations since each reaction is represented by a column in the stoichiometric coefficient matrix. Therefore,

$$(\mathcal{V}^{\mathrm{II}})^{\mathrm{T}} = \boldsymbol{D}(\mathcal{V}^{\mathrm{I}})^{\mathrm{T}}, \tag{B.1}$$

where $\boldsymbol{D}$ is a nonsingular permutation matrix (Strang, 1988, p. 215) of dimension (R, R) that produces the column operations.

From Eqs. (A.6) and (A.9), we can write the mole balances for the two reaction chemistries as

$$(\boldsymbol{n}^0 - \boldsymbol{n})^{\mathrm{I}} = \mathcal{V}^{\mathrm{I}}(\mathcal{V}^{\mathrm{I}}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}} - \boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{I}}, \tag{B.2}$$

$$(\boldsymbol{n}^0 - \boldsymbol{n})^{\mathrm{II}} = \mathcal{V}^{\mathrm{II}}(\mathcal{V}^{\mathrm{II}}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}} - \boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{II}}. \tag{B.3}$$

To prove that both reaction chemistries give equivalent mole balances, we must show that if $(\boldsymbol{n}^0)^{\mathrm{I}}$ is the same as $(\boldsymbol{n}^0)^{\mathrm{II}}$, then $(\boldsymbol{n})^{\mathrm{I}}$ is the same as $(\boldsymbol{n})^{\mathrm{II}}$. We accomplish this by showing that the RHS of Eqs. (B.2) and (B.3) are the same.

Step 1*:* Assuming we choose the same reference components for evaluating the mole balances for both the reaction chemistries, then we can always arrange that

$$(\boldsymbol{n}^0_{\mathrm{Ref}} - \boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{I}} = (\boldsymbol{n}^0_{\mathrm{Ref}} - \boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{II}}. \tag{B.4}$$

The degrees of freedom for mole balances are $c + R$ for each set of mole balances given in Eqs. (B.2) and (B.3), respectively. We set them as follows:

- $(n_i^0)^{\mathrm{I}} = (n_i^0)^{\mathrm{II}}, \quad i = 1, \ldots, c,$
- $(n_{i,\mathrm{Ref}})^{\mathrm{I}} = (n_{i,\mathrm{Ref}})^{\mathrm{II}}, \quad i = (c-R+1), \ldots, c.$

The reaction species are arranged in the same order for both the reaction chemistries. Therefore, Eq. (B.4) is satisfied by specifying the $c+R$ degrees of freedom.

Step 2*:* A matrix of stoichiometric coefficients for the reference components is a submatrix of the full stoichiometric coefficient matrix and, therefore, can be represented as

$$\mathcal{V}^{\mathrm{I}}_{\mathrm{Ref}} = \boldsymbol{B}\mathcal{V}^{\mathrm{I}}, \tag{B.5}$$

$$\mathcal{V}^{\mathrm{II}}_{\mathrm{Ref}} = \boldsymbol{B}\mathcal{V}^{\mathrm{II}}, \tag{B.6}$$

where $\boldsymbol{B}$ is a nonsquare matrix of dimension (R, c) given as

$$\boldsymbol{B} = (\boldsymbol{O}, \boldsymbol{I}).$$

Here, $\boldsymbol{O}$ is a zero matrix of dimension (R, $c-R$) and $\boldsymbol{I}$ is an identity matrix of dimension (R, R).

Step 3: From Eqs. (B.3) and (B.6), we get,

$$(\boldsymbol{n}^0-\boldsymbol{n})^{\mathrm{II}}=\mathscr{V}^{\mathrm{II}}(\boldsymbol{B}\mathscr{V}^{\mathrm{II}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}}-\boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{II}}. \tag{B.7}$$

Taking the transpose on both sides of Eq. (B.1), we have,

$$\mathscr{V}^{\mathrm{II}}=\mathscr{V}^{\mathrm{I}}\boldsymbol{D}^{\mathrm{T}}. \tag{B.8}$$

Substituting Eq. (B.8) in Eq. (B.7), and using Eqs. (B.4) and (B.5), we get,

$$(\boldsymbol{n}^0-\boldsymbol{n})^{\mathrm{II}}=\mathscr{V}^{\mathrm{I}}\boldsymbol{D}^{\mathrm{T}}(\boldsymbol{B}\mathscr{V}^{\mathrm{I}}\boldsymbol{D}^{\mathrm{T}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}}-\boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{II}}, \tag{B.9}$$

$$=\mathscr{V}^{\mathrm{I}}(\boldsymbol{B}\mathscr{V}^{\mathrm{I}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}}-\boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{II}}, \tag{B.10}$$

$$=\mathscr{V}^{\mathrm{I}}(\mathscr{V}^{\mathrm{I}}_{\mathrm{Ref}})^{-1}(\boldsymbol{n}^0_{\mathrm{Ref}}-\boldsymbol{n}_{\mathrm{Ref}})^{\mathrm{I}}, \tag{B.11}$$

$$=(\boldsymbol{n}^0-\boldsymbol{n})^{\mathrm{I}}. \tag{B.12}$$

Therefore, mole balances are equivalent for every set containing the maximum number of independent chemical equations. □

Appendix C. Proof of Corollary to Property 2

Corollary. *Element balances form a subset of the mole balances for less than the maximum number of independent reactions.*

Proof. Let $R_{\max}$ be the maximum number of independent reactions and R be the number of reactions (assume each is independent) for a set containing less than the maximum number of independent reactions, therefore, $R<R_{\max}$. The change in number of moles of c components while R reactions are proceeding is given by Eq. (A.6) as

$$\mathscr{V}\boldsymbol{\varepsilon}=(\boldsymbol{n}-\boldsymbol{n}^0), \tag{C.1}$$

where $\mathscr{V}$ is a stoichiometric coefficient matrix for a chemistry with R chemical equations. For given extents of reaction, $\boldsymbol{\varepsilon}^*$, we can determine $(\boldsymbol{n}-\boldsymbol{n}^0)^*$ as the solution to the above equation. For the case of the maximum number of independent chemical equations, $R_{\max}$, the element balances are (Schneider & Reklaitis, 1975)

$$\boldsymbol{A}(\boldsymbol{n}-\boldsymbol{n}^0)=0, \tag{C.2}$$

where $\boldsymbol{A}$ is the atomic matrix of dimension (e, c) and $\boldsymbol{0}$ is a zero vector of dimension e. There are $(c-R_{\max})$ independent element balances in this case, where $c-R_{\max}\leqslant e$. Since the R chemical equations given by $\mathscr{V}$ are stoichiometrically balanced, conservation of elemental species leads to,

$$\boldsymbol{A}\mathscr{V}=\boldsymbol{O}, \tag{C.3}$$

where $\boldsymbol{O}$ is a zero matrix of dimension (e, R). Now we check whether $(\boldsymbol{n}-\boldsymbol{n}^0)^*$, which solves C.1, also satisfies C.2. We check this by direct substitution of $(\boldsymbol{n}-\boldsymbol{n}^0)^*$ from C.1 into C.2, giving

$$\boldsymbol{A}(\boldsymbol{n}-\boldsymbol{n}^0)=\boldsymbol{A}\mathscr{V}\boldsymbol{\varepsilon}. \tag{C.4}$$

Using Eq. (C.3),

$$\boldsymbol{A}\mathscr{V}\boldsymbol{\varepsilon}=0. \tag{C.5}$$

Therefore, $(\boldsymbol{n}-\boldsymbol{n}^0)^*$ satisfies both Eq. (C.1) (mole balances) and Eq. (C.2) (element balances).

Eq. (C.1) corresponds to $(c-R)$ independent mole balances (Appendix A), and, Eq. (C.2) corresponds to $(c-R_{\max})$ independent element balances. Since, $R_{\max}>R$, the number of mole balances is greater than the number of element balances. Therefore, the element balances form a subset of the mole balances for less than the maximum number of independent reactions.

Appendix D. Independence of element balances

Consider a reaction system consisting of ethylene oxide (C_2H_4O), water (H_2O), ethylene glycol ($C_2H_6O_2$) and diethylene glycol ($C_4H_{10}O_3$). The species are numbered as follows: ethylene oxide (1), water (2), ethylene glycol (3) and diethylene glycol (4). The atomic matrix for the system is given as

$$\boldsymbol{A}=\begin{array}{c|cccc|} & (1) & (2) & (3) & (4) \\ C & 2 & 0 & 2 & 4 \\ H & 4 & 2 & 6 & 10 \\ O & 1 & 1 & 2 & 3 \end{array} \tag{D.1}$$

Each row of the atomic matrix represents an element balance given by the summation of the product of the coefficient in the row and the corresponding species at the top of the column. Performing elementary row operations and reducing the matrix **A** to its echelon form, we get

$$\boldsymbol{A}^*=\begin{array}{c|cccc|} & (1) & (2) & (3) & (4) \\ C & 1 & 0 & 1 & 2 \\ H & 0 & 1 & 1 & 1 \\ O & 0 & 0 & 0 & 0 \end{array} \tag{D.2}$$

The rank of matrix $\boldsymbol{A}$ is $\mathscr{R}=2$. There are $c-\mathscr{R}=2$ independent chemical reactions,

$$C_2H_4O+H_2O\rightleftharpoons C_2H_6O_2 \tag{D.3a}$$

$$C_2H_4O+C_2H_6O_2\rightleftharpoons C_4H_{10}O_3 \tag{D.3b}$$

Since $\mathscr{R}=2$, there are only two independent element balances for the reaction system. The row vectors of the elements in matrix **A** can be related as

$$C + 2O - H = 0 \quad (D.4)$$

Physically, it means that the constituent elements of each molecule are related to each other by a stoichiometric relationship D.4, and this relationship applies to each species in the system. Since there is one stoichiometric relationship between the elements for this reaction system, there is one less independent element balance. The concept of independence of element balances is discussed by Reklaitis (1983, Ch. 4). Reklaitis (1983, Example 4.5) considers an example with five chemical species (CO_2, H_2O, NH_3, $(NH_2)_2CO$, NH_2COONH_4) and involves four elements (C, H, O, N). One of the element balances for this system is dependent and the stoichiometric relationship between the elements is, $4C + H - 2O - 3N = 0$, which is satisfied by each of the species.

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