

Reaction Route Graphs. III. Non-Minimal Kinetic Mechanisms

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The concept of reaction route (RR) graphs introduced recently by us for kinetic mechanisms that produce minimal graphs is extended to the problem of non-minimal kinetic mechanisms for the case of a single overall reaction (OR). A RR graph is said to be minimal if all of the stoichiometric numbers in all direct RRs of the mechanism are equal to ± 1 and non-minimal if at least one stoichiometric number in a direct RR is non-unity, e.g., equal to ± 2 . For a given mechanism, four unique topological characteristics of RR graphs are defined and enumerated, namely, direct full routes (FRs), empty routes (ERs), intermediate nodes (INs), and terminal nodes (TNs). These are further utilized to construct the RR graphs. One algorithm involves viewing each IN as a central node in a RR sub-graph. As a result, the construction and enumeration of RR graphs are reduced to the problem of balancing the peripheral nodes in the RR sub-graphs according to the list of FRs, ERs, INs, and TNs. An alternate method involves using an independent set of RRs to draw the RR graph while satisfying the INs and TNs. Three examples are presented to illustrate the application of non-minimal RR graph theory.

Introduction

Graph theoretical methods have been used extensively to address a variety of topological problems in chemistry,^{1–8} including the topological description of complex chemical reaction networks (a full review of the subject may be found in ref 3). More recently,^{9,10} complex biochemical networks have been discussed in the context of a rather general mathematical network theory.¹¹ A universal feature of the graph-theoretical approach used so far for the topological description of chemical reaction networks has been that each node, or vertex, represents a *single* species, while the branches, or edges, represent the species connectivity according to the elementary reaction steps comprising the mechanism. Although the notion of associating the species with the nodes is intuitively appealing (being directly analogous to the conventional manner of depicting mechanisms in chemistry) and is a useful formalism for studying monomolecular reaction networks, this approach cannot be extended to the more general cases and leaves open a series of fundamental problems concerning complex chemical mechanisms. For example, the conventional reaction graphs cannot, in general, be used in a straightforward manner for kinetic analysis, reduction, and simplification.

In the two previous papers of this series,^{12,13} we have introduced a new type of reaction network referred to as the reaction route (RR) graph. The main idea behind RR graph theory is to associate the branches directly with the elementary reaction steps and simply require the nodes to represent the connectivity of reaction steps and to satisfy the quasi-steady-state conditions for the intermediates and terminal species. As a result, all of the RRs for the system can then be traced simply as paths on the RR graph. It was shown that this new type of graph represents a powerful tool in studying complex, nonlinear kinetic mechanisms. Another major advantage of the new RR graph approach is that there exists a direct analogy between the RR graphs and electrical networks, which provides a

powerful new set of tools for kinetic analysis, including Kirchhoff's laws. So far, however, we have considered only minimal RR graphs,^{12,13} e.g., RR graphs in which every elementary reaction step is presented only once in each enumerated RR, i.e., only unit stoichiometric numbers are involved. However, the vast majority of kinetic mechanisms involve non-unit stoichiometric numbers in many RRs. These mechanisms are represented by non-minimal RR graphs, e.g., RR graphs in which an elementary reaction step may be present in the graph more than once, i.e., in different locations of the graph, corresponding to the non-unit stoichiometric numbers. The purpose of the present communication is to extend the concept of RR graphs to this more general case of the non-minimal RR graphs. The discussion here, however, is limited to the case of a single overall reaction (OR).

Notation and Definitions

We consider the general case of a chemical reaction system described by a reaction mechanism comprising p elementary reaction steps s_ρ ($\rho = 1, 2, \dots, p$). The species involved in the elementary reaction steps are divided into l intermediates I_1, I_2, \dots, I_l , of which q are independent, and n terminal species (reactants and products) T_1, T_2, \dots, T_n . Thus, the elementary reaction steps may be presented as

$$s_\rho: \sum_{k=1}^l \alpha_{\rho k} I_k + \sum_{i=1}^n \beta_{\rho i} T_i = 0 \quad (\rho = 1, 2, \dots, p) \quad (1)$$

By convention, the stoichiometric coefficients of the intermediates $\alpha_{\rho k}$ ($\rho = 1, 2, \dots, p; k = 1, 2, \dots, l$) and terminal species $\beta_{\rho i}$ ($\rho = 1, 2, \dots, p; i = 1, 2, \dots, n$) are assumed to be positive for products and negative for reactants. For simplicity, we assume that the overall chemical process is described by only one overall reaction (OR):

$$\text{OR:} \quad \nu_1 T_1 + \nu_2 T_2 + \dots + \nu_n T_n = 0 \quad (2)$$

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The columns in the stoichiometric matrix of the mechanism, now defined without the OR,

$$\mathbf{v} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1l} & \beta_{11} & \beta_{12} & \dots & \beta_{1n} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2l} & \beta_{21} & \beta_{22} & \dots & \beta_{2n} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{p1} & \alpha_{p2} & \dots & \alpha_{pl} & \beta_{p1} & \beta_{p2} & \dots & \beta_{pn} \end{bmatrix} \quad (3)$$

are, in general, linearly dependent. For our purpose, it is necessary to define, as follows, two submatrices of \mathbf{v} in which the columns are linearly independent. First, we observe that the columns in the two submatrices comprising the intermediates and terminal species may be linearly dependent; that is,

$$\text{rank } \boldsymbol{\alpha}' = \text{rank} \begin{bmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1l} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2l} \\ \dots & \dots & \dots & \dots \\ \alpha_{p1} & \alpha_{p2} & \dots & \alpha_{pl} \end{bmatrix} = q \leq l \quad (4)$$

$$\text{rank } \boldsymbol{\beta}' = \text{rank} \begin{bmatrix} \beta_{11} & \beta_{12} & \dots & \beta_{1n} \\ \beta_{21} & \beta_{22} & \dots & \beta_{2n} \\ \dots & \dots & \dots & \dots \\ \beta_{p1} & \beta_{p2} & \dots & \beta_{pn} \end{bmatrix} = t \leq n \quad (5)$$

In such cases, the linearly dependent columns in $\boldsymbol{\alpha}'$ may be omitted. Without loss of generality, we assume that the first q columns in $\boldsymbol{\alpha}'$ are linearly independent and define the submatrix

$$\boldsymbol{\alpha} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1q} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2q} \\ \dots & \dots & \dots & \dots \\ \alpha_{p1} & \alpha_{p2} & \dots & \alpha_{pq} \end{bmatrix} \quad (6)$$

so that $\text{rank } \boldsymbol{\alpha} = q$. In what follows, the submatrix $\boldsymbol{\alpha}$ is referred to as the *intermediate* submatrix. Next, we notice that the rank of the stoichiometric matrix \mathbf{v} is equal to $q + 1$. Without loss of generality, we eliminate the last $n - 1$ columns from $\boldsymbol{\beta}'$ and define a *reduced* stoichiometric submatrix

$$\boldsymbol{\gamma} = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1q} & \beta_{11} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2q} & \beta_{21} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{p1} & \alpha_{p2} & \dots & \alpha_{pq} & \beta_{p1} \end{bmatrix} \quad (7)$$

such that $\text{rank } \mathbf{v} = \text{rank } \boldsymbol{\gamma} = q + 1$.

We define, further, the rate and dimensionless affinity vectors

$$\mathbf{r} = (r_1, r_2, \dots, r_p)^T \quad (8)$$

$$\mathcal{A} = (\mathcal{A}_1, \mathcal{A}_2, \dots, \mathcal{A}_p)^T \quad (9)$$

where r_ρ ($\rho = 1, 2, \dots, p$) and \mathcal{A}_ρ ($\rho = 1, 2, \dots, p$) are the rates and dimensionless affinities of the elementary reaction steps. By definition,¹² r_ρ and \mathcal{A}_ρ are interrelated via the De Donder relation:

$$r_\rho = \bar{r}_\rho - \bar{r}_\rho \quad (10)$$

$$\mathcal{A}_\rho = \frac{A_\rho}{RT} = \ln \frac{\bar{r}_\rho}{r_\rho} \quad (11)$$

where A_ρ is the affinity of elementary reaction step s_ρ ¹², while \bar{r}_ρ and \bar{r}_ρ represent the rates of the elementary reaction steps in the forward and backward direction, respectively.

Finally, we assume that the rates of formation and consumption of the intermediates are approximately equal and, hence, the quasi-steady-state (QSS) approximation holds. Thus, we introduce the vector

$$\mathbf{Q} = (Q_1, Q_2, \dots, Q_q)^T \quad (12)$$

where the Q_k 's ($k = 1, 2, \dots, q$) denote the QSS conditions of the linearly independent intermediates I_k ($k = 1, 2, \dots, q$). The QSS conditions of the linearly independent intermediates may be written in vector form as

$$\mathbf{Q}: \quad \boldsymbol{\alpha}^T \mathbf{r} = 0 \quad (13)$$

or

$$Q_1: \quad \alpha_{11}r_1 + \alpha_{21}r_2 + \dots + \alpha_{p1}r_p = 0$$

$$Q_2: \quad \alpha_{12}r_1 + \alpha_{22}r_2 + \dots + \alpha_{p2}r_p = 0$$

...

$$Q_q: \quad \alpha_{1q}r_1 + \alpha_{2q}r_2 + \dots + \alpha_{pq}r_p = 0 \quad (14)$$

In what follows, eq 14 is referred to as the *intermediate* QSS conditions. On the other hand, the rate r_{OR} of the OR under QSS conditions is related to the rates of the elementary reaction steps via

$$r_{\text{OR}} = \frac{1}{\nu_1} \sum_{\rho=1}^p \beta_{\rho 1} r_\rho = \frac{1}{\nu_2} \sum_{\rho=1}^p \beta_{\rho 2} r_\rho = \dots = \frac{1}{\nu_n} \sum_{\rho=1}^p \beta_{\rho n} r_\rho \quad (15)$$

where r_ρ ($\rho = 1, 2, \dots, p$) are subject to the intermediate QSS conditions, eq 14. Furthermore, eq 15 is referred to as the OR QSS conditions.

Reaction Routes

In the most general case, a reaction route (RR) is defined as a linear combination of the elementary reaction steps s_1, s_2, \dots, s_p that eliminates a specified number of species (intermediates and terminal species) and produces an OR.^{14,15} The coefficients of s_ρ in this linear combination $\sigma_1, \sigma_2, \dots, \sigma_p$ are called stoichiometric numbers. Depending upon the resulting net reaction produced by a RR, we distinguish among three types of RRs.

i. Full RRs. A RR that eliminates *all* intermediates while retaining *only* the terminal species, thus, producing an OR, is referred to as a *full* RR or, simply, FR. Mathematically, the g th FR is defined as

$$\text{FR}_g: \quad \sum_{\rho=1}^p \sigma_{g\rho} s_\rho = \text{OR} \quad (16)$$

The FR_g , that is, a set of stoichiometric numbers $\sigma_{g1}, \sigma_{g2}, \dots, \sigma_{gp}$, may be generated based on the following considerations. Substituting eq 1 into eq 16, we have

$$\sum_{\rho=1}^p \sigma_{g\rho} \left(\sum_{k=1}^l \alpha_{\rho k} I_k + \sum_{i=1}^n \beta_{\rho i} T_i \right) = \sum_{k=1}^l \left(\sum_{\rho=1}^p \sigma_{g\rho} \alpha_{\rho k} \right) I_k + \sum_{i=1}^n \left(\sum_{\rho=1}^p \sigma_{g\rho} \beta_{\rho i} \right) T_i = \text{OR} \quad (17)$$

By definition, the intermediates in a FR should vanish. That is,

$$\sum_{\rho=1}^p \alpha_{\rho k} \sigma_{g\rho} = 0 \quad (k = 1, 2, \dots, l)$$

or

$$\alpha'^T \sigma_g = 0$$

where σ_g is the vector of stoichiometric numbers

$$\sigma_g = (\sigma_{g1}, \sigma_{g2}, \dots, \sigma_{gp})^T \quad (18)$$

After removing the linearly dependent columns in α' , we have

$$\alpha^T \sigma_g = 0 \quad (19)$$

Thus, σ_g may be determined by solving a system of homogeneous linear equations, e.g., eq 19. The number of linearly independent FRs is equal to $p - \text{rank } \alpha = p - q$.

ii. Empty RRs. A RR that eliminates *all species*, both intermediate and terminal species, thus producing a reaction in which all of the stoichiometric coefficients of the species are equal to zero (called a *zero reaction*) is referred to as an *empty* RR or, simply, an *empty route* (ER). Mathematically, the g th ER is defined as

$$\text{ER}_g: \sum_{\rho=1}^p \sigma_{g\rho} s_{\rho} = 0 \quad (20)$$

Substituting eq 1 into eq 20 and requiring all of the species to vanish, we have

$$\sum_{\rho=1}^p \alpha_{\rho k} \sigma_{g\rho} = 0 \quad (k = 1, 2, \dots, l)$$

$$\sum_{\rho=1}^p \beta_{\rho i} \sigma_{g\rho} = 0 \quad (i = 1, 2, \dots, n)$$

or

$$\nu^T \sigma_g = 0$$

Eliminating the linearly dependent columns from the stoichiometric matrix ν gives

$$\gamma^T \sigma_g = 0 \quad (21)$$

Thus, the ERs are also generated by solving a set of homogeneous linear equations, e.g., eq 21. The number of linearly independent ERs is equal to $p - \text{rank } \nu = p - (q + 1)$.

iii. Intermediate RRs. A RR that eliminates *only some* of the intermediate and terminal species, thus, producing an *intermediate overall reaction* (IOR), that is, a reaction involving both terminal and intermediate species is referred to as an *intermediate* RR or, simply, an *intermediate route* (IR). Mathematically, the g th IR is defined as

$$\text{IR}_g: \sigma_{g1}s_1 + \sigma_{g2}s_2 + \dots + \sigma_{gp}s_p = \text{IOR} \quad (22)$$

The IRs may be generated by solving a system of homogeneous linear equations similar to those described above. The explicit form of this system depends on the list of species that are either involved in or eliminated from the IOR.

One of the important tasks of the theory of RRs is to generate a set of linearly independent RRs. Since this set may be

generated arbitrarily, it may involve both FRs and ERs provided at least one of the RRs is a FR. According to the Horiuti–Temkin theorem,^{14,15} the number of linearly independent RRs is equal to $p - \text{rank } \alpha = p - q$. The latter can be generated by solving eq 19. In particular, a set of linearly independent RRs may be generated as follows. First, we select a subset of q linearly independent elementary reaction steps. Without loss of generality, we assume that these are the first q steps. Because the first q elementary reaction steps were assumed to be linearly independent, we have

$$\sigma = \begin{vmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1q} \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2q} \\ \dots & \dots & \dots & \dots \\ \alpha_{q1} & \alpha_{q2} & \dots & \alpha_{qq} \end{vmatrix} \neq 0 \quad (23)$$

Next, we form $(p - q)$ subsets of $(q + 1)$ elementary reactions by adding one of the remaining elementary reaction steps s_{q+j} ($j = 1, 2, \dots, p - q$) to the first q . Each of these $(p - q)$ sets of $(q + 1)$ elementary reaction steps $\{s_1, s_2, \dots, s_q, s_{q+j}\}$ ($j = 1, 2, \dots, p - q$) may be either linearly dependent or independent. Namely, if $\{s_1, s_2, \dots, s_q, s_{q+j}\}$ are linearly independent, the resulting RR is a FR, and if $\{s_1, s_2, \dots, s_q, s_{q+j}\}$ are linearly dependent, the resulting RR is an ER. Such a selection of the elementary reactions ensures that the fundamental RR matrix is of the form^{12,16}

$$\sigma_f = (\sigma_1^T, \sigma_2^T, \dots, \sigma_{p-q}^T) = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \dots & \sigma_{1q} & \sigma & 0 & \dots & 0 \\ \sigma_{21} & \sigma_{22} & \dots & \sigma_{2q} & 0 & \sigma & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \sigma_{p-q,1} & \sigma_{p-q,2} & \dots & \sigma_{p-q,q} & 0 & 0 & \dots & \sigma \end{bmatrix} \quad (24)$$

now without the OR, where

$$\sigma_{jk} = \begin{vmatrix} \alpha_{11} & \alpha_{12} & \dots & \alpha_{1q} & 0 \\ \alpha_{21} & \alpha_{22} & \dots & \alpha_{2q} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{k-1,1} & \alpha_{k-1,2} & \dots & \alpha_{k-1,q} & 0 \\ \alpha_{k1,1} & \alpha_{k2} & \dots & \alpha_{kq} & 1 \\ \alpha_{k+1,1} & \alpha_{k+1,2} & \dots & \alpha_{k+1,q} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{q1} & \alpha_{q2} & \dots & \alpha_{qq} & 0 \\ \alpha_{q+j,1} & \alpha_{q+j,2} & \dots & \alpha_{q+j,q} & 0 \end{vmatrix} \quad (k = 1, 2, \dots, q; j = 1, 2, \dots, p - q) \quad (25)$$

For many mechanisms (but not all), the subset of q linearly independent elementary reaction steps may be selected such that $\sigma = +1$. It is also possible to select the subset of q linearly independent elementary reaction steps so that only one RR is a FR while the remaining are ERs. For our purposes, it is convenient to select these as the shortest RRs.

Direct Reaction Routes

If the RRs are not subject to any further constraints, the vectors of stoichiometric numbers σ_g may be generated arbitrarily. This arbitrariness of the RRs may be avoided if, following Milner¹⁷ and Happel and Sellers,¹⁸ it is required that RRs be direct. The “direct” RRs are minimal in the sense that, if an elementary reaction step is omitted from the RR, it is not possible to eliminate all of the specified species by linearly combining the remaining elementary reaction step. We define, further, two types of direct RRs.

Direct FRs. According to Milner,¹⁷ a direct FR involves no more than rank $\alpha + 1 = q + 1$ linearly independent elementary reaction steps. Let the $q + 1$ linearly independent elementary reaction steps that are involved in a direct FR be $s_{i_1}, s_{i_2}, \dots, s_{i_q}, s_{i_{q+1}}$, where the subscripts $i_1, i_2, \dots, i_q, i_{q+1}$ represent an ordered set of $q + 1$ integers from among the p elementary steps, that is, $1 \leq i_1 < i_2 < \dots < i_q < i_{q+1} \leq p$. A direct FR may be denoted by $\text{FR}(s_{i_1}, s_{i_2}, \dots, s_{i_q}, s_{i_{q+1}})$, thus, specifying the elementary reaction steps $s_{i_1}, s_{i_2}, \dots, s_{i_q}, s_{i_{q+1}}$ that are involved in the FR. Thus, in general,

$$\text{FR}(s_{i_1}, s_{i_2}, \dots, s_{i_q}, s_{i_{q+1}}):$$

$$\sigma_{i_1} s_{i_1} + \sigma_{i_2} s_{i_2} + \dots + \sigma_{i_q} s_{i_q} + \sigma_{i_{q+1}} s_{i_{q+1}} = \text{OR} \quad (26)$$

where the stoichiometric numbers $\sigma_{gi_1}, \sigma_{gi_2}, \dots, \sigma_{gi_q}, \sigma_{gi_{q+1}}$ are obtained by solving eq 19. As shown earlier by us,¹⁶ the solution is

$$\sigma_{i_k} = \begin{vmatrix} \alpha_{i_1,1} & \alpha_{i_1,2} & \dots & \alpha_{i_1,q} & 0 \\ \alpha_{i_2,1} & \alpha_{i_2,2} & \dots & \alpha_{i_2,q} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{i_{k-1},1} & \alpha_{i_{k-1},2} & \dots & \alpha_{i_{k-1},q} & 0 \\ \alpha_{i_k,1} & \alpha_{i_k,2} & \dots & \alpha_{i_k,q} & 1 \\ \alpha_{i_{k+1},1} & \alpha_{i_{k+1},2} & \dots & \alpha_{i_{k+1},q} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{i_q,1} & \alpha_{i_q,2} & \dots & \alpha_{i_q,q} & 0 \\ \alpha_{i_{q+1},1} & \alpha_{i_{q+1},2} & \dots & \alpha_{i_{q+1},q} & 0 \end{vmatrix} \quad (27)$$

More succinctly, the general equation of a FR may, thus, be written as

$$\text{FR}(s_{i_1}, s_{i_2}, \dots, s_{i_q}, s_{i_{q+1}}):$$

$$\begin{vmatrix} \alpha_{i_1,1} & \alpha_{i_1,2} & \dots & \alpha_{i_1,q} & s_{i_1} \\ \alpha_{i_2,1} & \alpha_{i_2,2} & \dots & \alpha_{i_2,q} & s_{i_2} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{i_q,1} & \alpha_{i_q,2} & \dots & \alpha_{i_q,q} & s_{i_q} \\ \alpha_{i_{q+1},1} & \alpha_{i_{q+1},2} & \dots & \alpha_{i_{q+1},q} & s_{i_{q+1}} \end{vmatrix} = \text{OR} \quad (28)$$

The affinity A_{OR} of the OR is related to the affinities $A_{i_1}, A_{i_2}, \dots, A_{i_q}, A_{i_{q+1}}$ of the elementary reaction steps comprising a direct FR via Kirchhoff's voltage law (KVL); that is,

$$A_{\text{OR}} = \sigma_{i_1} A_{i_1} + \sigma_{i_2} A_{i_2} + \dots + \sigma_{i_q} A_{i_q} + \sigma_{i_{q+1}} A_{i_{q+1}} \quad (29)$$

or, employing eq 27,

$$A_{\text{OR}} = \begin{vmatrix} \alpha_{i_1,1} & \alpha_{i_1,2} & \dots & \alpha_{i_1,q} & A_{i_1} \\ \alpha_{i_2,1} & \alpha_{i_2,2} & \dots & \alpha_{i_2,q} & A_{i_2} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{i_q,1} & \alpha_{i_q,2} & \dots & \alpha_{i_q,q} & A_{i_q} \\ \alpha_{i_{q+1},1} & \alpha_{i_{q+1},2} & \dots & \alpha_{i_{q+1},q} & A_{i_{q+1}} \end{vmatrix} \quad (30)$$

Clearly, not every subset of $q + 1$ elementary reaction steps from the total of p is linearly independent. Also, not every subset of $q + 1$ linearly independent elementary reaction steps will necessarily result in a distinct RR. For instance, some steps (e.g., adsorption, desorption) may be involved in all FRs. Further, some of the stoichiometric numbers in different FRs may equal

zero, thus, resulting in a smaller number of distinct FRs. The direct FRs may alternately be generated employing another appropriate method, for example, that of Happel and Sellers¹⁸ or Fishtik and Datta.¹⁶ Alternatively, the direct FRs may be enumerated by considering all of the possible choices of $q + 1$ elementary reaction steps from among the total of p . The number of stoichiometrically distinct direct FRs enumerated, however, usually far exceeds $p - q$, the number of linearly independent FRs.

Direct ERs. The concept of directness may be extended to ERs. Thus, by analogy with a direct FR, we define a *direct* ER as a RR that involves no more than rank $\gamma + 1 = q + 2$ elementary reaction steps, where γ is the reduced stoichiometric matrix, eq 7. Let the $q + 2$ elementary reaction steps that are involved in an ER be $s_{j_1}, s_{j_2}, \dots, s_{j_q}, s_{j_{q+1}}, s_{j_{q+2}}$, where the subscripts $j_1, j_2, \dots, j_q, j_{q+1}, j_{q+2}$ represent an ordered set of $q + 2$ integers from among p satisfying the condition $1 \leq j_1 < j_2 < \dots < j_q < j_{q+1} < j_{q+2} \leq p$. A direct ER is denoted by $\text{ER}(s_{j_1}, s_{j_2}, \dots, s_{j_q}, s_{j_{q+1}}, s_{j_{q+2}})$, thus, specifying the elementary reaction steps $s_{j_1}, s_{j_2}, \dots, s_{j_q}, s_{j_{q+1}}, s_{j_{q+2}}$ that are involved in the ER. Thus, in general,

$$\text{ER}(s_{j_1}, s_{j_2}, \dots, s_{j_q}, s_{j_{q+1}}, s_{j_{q+2}}):$$

$$\sigma_{j_1} s_{j_1} + \sigma_{j_2} s_{j_2} + \dots + \sigma_{j_q} s_{j_q} + \sigma_{j_{q+1}} s_{j_{q+1}} + \sigma_{j_{q+2}} s_{j_{q+2}} = 0 \quad (31)$$

where the stoichiometric numbers are obtained by solving eq 21. The solution is

$$\sigma_{j_k} = \begin{vmatrix} \alpha_{j_1,1} & \alpha_{j_1,2} & \dots & \alpha_{j_1,q} & \beta_{j_1,1} & 0 \\ \alpha_{j_2,1} & \alpha_{j_2,2} & \dots & \alpha_{j_2,q} & \beta_{j_2,1} & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{j_{k-1},1} & \alpha_{j_{k-1},2} & \dots & \alpha_{j_{k-1},q} & \beta_{j_{k-1},1} & 0 \\ \alpha_{j_k,1} & \alpha_{j_k,2} & \dots & \alpha_{j_k,q} & \beta_{j_k,1} & 1 \\ \alpha_{j_{k+1},1} & \alpha_{j_{k+1},2} & \dots & \alpha_{j_{k+1},q} & \beta_{j_{k+1},1} & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{j_q,1} & \alpha_{j_q,2} & \dots & \alpha_{j_q,q} & \beta_{j_q,1} & 0 \\ \alpha_{j_{q+1},1} & \alpha_{j_{q+1},2} & \dots & \alpha_{j_{q+1},q} & \beta_{j_{q+1},1} & 0 \\ \alpha_{j_{q+2},1} & \alpha_{j_{q+2},2} & \dots & \alpha_{j_{q+2},q} & \beta_{j_{q+2},1} & 0 \end{vmatrix} \quad (32)$$

Alternatively, this result may be represented as

$$\text{ER}(s_{j_1}, s_{j_2}, \dots, s_{j_q}, s_{j_{q+1}}, s_{j_{q+2}}):$$

$$\begin{vmatrix} \alpha_{j_1,1} & \alpha_{j_1,2} & \dots & \alpha_{j_1,q} & \beta_{j_1,1} & s_{j_1} \\ \alpha_{j_2,1} & \alpha_{j_2,2} & \dots & \alpha_{j_2,q} & \beta_{j_2,1} & s_{j_2} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{j_q,1} & \alpha_{j_q,2} & \dots & \alpha_{j_q,q} & \beta_{j_q,1} & s_{j_q} \\ \alpha_{j_{q+1},1} & \alpha_{j_{q+1},2} & \dots & \alpha_{j_{q+1},q} & \beta_{j_{q+1},1} & s_{j_{q+1}} \\ \alpha_{j_{q+2},1} & \alpha_{j_{q+2},2} & \dots & \alpha_{j_{q+2},q} & \beta_{j_{q+2},1} & s_{j_{q+2}} \end{vmatrix} = 0 \quad (33)$$

Because an ER produces a zero net reaction, the affinities of the elementary reaction steps $A_{j_1}, A_{j_2}, \dots, A_{j_q}, A_{j_{q+1}}, A_{j_{q+2}}$ comprising an ER are subject to the following KVL constraint:

$$\sigma_{j_1} A_{j_1} + \sigma_{j_2} A_{j_2} + \dots + \sigma_{j_q} A_{j_q} + \sigma_{j_{q+1}} A_{j_{q+1}} + \sigma_{j_{q+2}} A_{j_{q+2}} = 0 \quad (34)$$

or, employing eq 32,

$$\begin{vmatrix} \alpha_{j_1,1} & \alpha_{j_1,2} & \dots & \alpha_{j_1,q} & \beta_{j_1,1} & A_{j_1} \\ \alpha_{j_2,1} & \alpha_{j_2,2} & \dots & \alpha_{j_2,q} & \beta_{j_2,1} & A_{j_2} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{j_q,1} & \alpha_{j_q,2} & \dots & \alpha_{j_q,q} & \beta_{j_q,1} & A_{j_q} \\ \alpha_{j_{q+1},1} & \alpha_{j_{q+1},2} & \dots & \alpha_{j_{q+1},q} & \beta_{j_{q+1},1} & A_{j_{q+1}} \\ \alpha_{j_{q+2},1} & \alpha_{j_{q+2},2} & \dots & \alpha_{j_{q+2},q} & \beta_{j_{q+2},1} & A_{j_{q+2}} \end{vmatrix} = 0 \quad (35)$$

Again, not necessarily every subset of $q + 2$ elementary reaction steps will result in a distinct ER. A complete set of distinct ERs may be generated either by considering all of the possible combinations of $q + 2$ elementary reaction steps from among the total of p or by appropriately modifying the method of Fishtik and Datta.¹⁶

Direct QSS Conditions and Direct Nodes

The nodes of the RR graph are subject to Kirchhoff's Current Law (KCL), e.g., the rates of the elementary reaction steps leaving and entering the nodes satisfy the intermediate and OR QSS conditions, eqs 14 and 15. It is necessary to distinguish between two different types of nodes. Thus, the nodes that satisfy the intermediate QSS conditions are referred to as the *intermediate nodes* (INs), while those that satisfy the OR QSS conditions are referred to as *terminal nodes* (TNs). It is to be further noted that nodes denote reaction connectivity. Therefore, an alternate definition of INs is that they represent exclusively the connectivity of the elementary reaction steps, while TNs also involve ORs. Furthermore, the QSS is a limiting form of KCL, which actually applies to non-steady-state conditions as well. Still, another interpretation is that INs represent only intermediate species, while the TNs also involve terminal species.

In general, the intermediate QSS conditions at the INs do not simply represent the QSS conditions of individual intermediate species, i.e., Q_1, Q_2, \dots, Q_q , eq 14. Rather, the QSS conditions at the INs, in general, represent a group of species, i.e., they represent a certain linear combination of Q_1, Q_2, \dots, Q_q . Since the linear combinations of Q_1, Q_2, \dots, Q_q may be arbitrary and, hence, infinite, so might be the number of INs. Similarly, the OR QSS conditions at the TNs do not necessarily coincide with those given by eq 15. Thus, eq 15 may be transformed using eq 14. As a result, the OR QSS conditions at the TNs may take a large variety of forms.

Clearly, to generate meaningful RR graphs, it is necessary to specify the rules that govern the connectivity of the elementary reaction steps at both the INs and TNs. In doing so, we accept the concept of directness in the sense that it has been defined and applied above to the RRs. More specifically, we assume that the number of elementary reaction steps connected at a direct node, either IN or TN, should be *minimal* in the sense that if a reaction is dropped from the node, it is not possible to satisfy the QSS conditions for the given set of species at that node by employing only the remaining reaction steps. In other words, it is postulated that *only the nodes that connect a minimum number of reaction steps satisfying the QSS conditions for a given set of species are allowed*. By analogy with RRs, the QSS conditions involving a minimal number of rates of the elementary reaction steps in the sense defined above are called *direct QSS conditions*, while the corresponding nodes are called *direct INs* and *direct TNs*.

Direct INs. The generation and enumeration of direct QSS conditions, or direct nodes, may be accomplished by employing the response reactions (RERs) formalism.¹⁹ Consider first the

enumeration of the direct intermediate QSS conditions. Let an arbitrary linear combination of the intermediate QSS conditions Q_1, Q_2, \dots, Q_q be

$$Q = \lambda_1 Q_1 + \lambda_2 Q_2 + \dots + \lambda_q Q_q = (\alpha_{11}r_1 + \alpha_{21}r_2 + \dots + \alpha_{p1}r_p)\lambda_1 + (\alpha_{12}r_1 + \alpha_{22}r_2 + \dots + \alpha_{p2}r_p)\lambda_2 + \dots + (\alpha_{1q}r_1 + \alpha_{2q}r_2 + \dots + \alpha_{pq}r_p)\lambda_q = 0 \quad (36)$$

where $\lambda_1, \lambda_2, \dots, \lambda_q$ are constants corresponding to the intermediate species. Now, to obtain the direct QSS conditions, i.e., those that involve a minimum number of rates, the constants $\lambda_1, \lambda_2, \dots, \lambda_q$ should be chosen so as to eliminate a maximum number of rates. This results in a system of homogeneous equations in the unknowns $\lambda_1, \lambda_2, \dots, \lambda_q$. As well-known from linear algebra, to obtain a nontrivial solution for $\lambda_1, \lambda_2, \dots, \lambda_q$, it is necessary to have no more than $q - 1$ linear homogeneous equations. That is, the intermediate QSS conditions Q_1, Q_2, \dots, Q_q should be linearly combined so as to eliminate at least $q - 1$ rates. In turn, this means that a direct intermediate QSS condition should involve no more than $p - (q - 1) = p - q + 1$ rates. This, of course, specifies the maximum degree of an intermediate node.²⁰

Let us partition the set of rates $\{r_1, r_2, \dots, r_p\}$ of the elementary reaction steps into two subsets: a subset of $q - 1$ rates $\{r_{l_1}, r_{l_2}, \dots, r_{l_{q-1}}\}$ ($1 \leq l_1 < l_2 < \dots < l_{q-1} \leq p$) that are *not involved* in a direct intermediate QSS condition and a subset of $p - q + 1$ rates $\{r_{h_1}, r_{h_2}, \dots, r_{h_{p-q+1}}\}$ ($1 \leq h_1 < h_2 < \dots < h_{p-q+1} \leq p$) that are *involved* in a direct QSS condition. Here $\{l_1, l_2, \dots, l_{q-1}\}$ and $\{h_1, h_2, \dots, h_{p-q+1}\}$ are two ordered subsets of integers chosen such that

$$\{l_1, l_2, \dots, l_{q-1}\} \cup \{h_1, h_2, \dots, h_{p-q+1}\} = \{1, 2, \dots, p\} \quad (37)$$

A direct intermediate QSS may, thus, be characterized by either the selection of $q - 1$ rates $r_{l_1}, r_{l_2}, \dots, r_{l_{q-1}}$ that are *not involved* or the $p - q + 1$ rates $\{r_{h_1}, r_{h_2}, \dots, r_{h_{p-q+1}}\}$ that are *involved* in a direct intermediate QSS. We denote a direct intermediate QSS condition by $Q(r_{h_1}, r_{h_2}, \dots, r_{h_{p-q+1}})$, thus, specifying the rates of the elementary reaction steps that are involved in a direct intermediate QSS condition. The latter may be obtained by choosing $\lambda_1, \lambda_2, \dots, \lambda_q$ in eq 36 so as to eliminate the rates $r_{l_1}, r_{l_2}, \dots, r_{l_{q-1}}$. This gives

$$\begin{aligned} \alpha_{l_1,1}\lambda_1 + \alpha_{l_1,2}\lambda_2 + \dots + \alpha_{l_1,q}\lambda_q &= 0 \\ \alpha_{l_2,1}\lambda_1 + \alpha_{l_2,2}\lambda_2 + \dots + \alpha_{l_2,q}\lambda_q &= 0 \\ \dots & \\ \alpha_{l_{q-1},1}\lambda_1 + \alpha_{l_{q-1},2}\lambda_2 + \dots + \alpha_{l_{q-1},q}\lambda_q &= 0 \end{aligned} \quad (38)$$

The solution to this system of homogeneous linear equations is

$$\lambda_k = \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_{q-1},1} & 0 \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_{q-1},2} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,k-1} & \alpha_{l_2,k-1} & \dots & \alpha_{l_{q-1},k-1} & 0 \\ \alpha_{l_1,k} & \alpha_{l_2,k} & \dots & \alpha_{l_{q-1},k} & 1 \\ \alpha_{l_1,k+1} & \alpha_{l_2,k+1} & \dots & \alpha_{l_{q-1},k+1} & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_{q-1},q} & 0 \end{vmatrix} \quad (k = 1, 2, \dots, q) \quad (39)$$

Substituting eq 39 into eq 36 gives the following general formula for a direct intermediate QSS condition:

$$Q(r_{h_1}, r_{h_2}, \dots, r_{h_{p-q+1}}):$$

$$\begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_{q-1},1} & Q_1 \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_{q-1},2} & Q_2 \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_{q-1},q} & Q_q \end{vmatrix} = 0 \quad (40)$$

or, taking into account eq 14, the direct QSS condition (KCL) for a node is

$$Q(r_{h_1}, r_{h_2}, \dots, r_{h_{p-q+1}}):$$

$$\sum_{k=1}^{p-q+1} \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_{q-1},1} & \alpha_{h_k,1} \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_{q-1},2} & \alpha_{h_k,2} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_{q-1},q} & \alpha_{h_k,q} \end{vmatrix} r_{h_k} = 0 \quad (41)$$

As a result, the general connectivity of an IN denoted by $n_I(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q+1}})$ is

$$n_I(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q+1}}):$$

$$\sum_{k=1}^{p-q+1} \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_{q-1},1} & \alpha_{h_k,1} \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_{q-1},2} & \alpha_{h_k,2} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_{q-1},q} & \alpha_{h_k,q} \end{vmatrix} s_{h_k} \quad (42)$$

The complete enumeration of direct intermediate QSS conditions and INs may be, in principle, performed by considering all of the possible combinations of $p - q + 1$ species from the total of p . Normally, the number of direct INs exceeds the number of linearly independent INs, that is, the number of linearly independent intermediates q . It may be noted again that although the node connectivity (eq 42) results from the QSS condition, it is more generally valid including the unsteady state.

Direct TNs. Now, consider the enumeration of the direct OR QSS conditions, that is, the enumeration of direct TNs. Since, again, a direct OR QSS condition should involve a minimum number of rates, it is necessary to eliminate from eq 15 the maximum number of rates by employing the interrelationships provided by the intermediate QSS, eq 14. Because rank $\alpha = q$, we can solve eq 14 for no more than q rates. Upon substitution of these q rates into eq 15, we arrive at a direct OR QSS condition involving no more than $p - q$ rates of the elementary reaction steps. Let $\{r_{l_1}, r_{l_2}, \dots, r_{l_q}\}$ ($1 \leq l_1 < l_2 < \dots < l_q \leq p$) be the q rates of the elementary reaction steps that are not involved in a direct OR QSS condition, while $\{r_{h_1}, r_{h_2}, \dots, r_{h_{p-q}}\}$ ($1 \leq h_1 < h_2 < \dots < h_{p-q} \leq p$) be the $p - q$ rates that are involved in a direct OR QSS condition. Here $\{l_1, l_2, \dots, l_q\}$ and $\{h_1, h_2, \dots, h_{p-q}\}$ are two ordered subsets of integers chosen so as to satisfy eq 37. A direct OR QSS condition is denoted by $P(r_{h_1}, r_{h_2}, \dots, r_{h_{p-q}})$ thus specifying the rates that are involved in a direct OR QSS condition. Its general equation may be obtained by solving eq 14 with respect to $\{r_{l_1}, r_{l_2}, \dots, r_{l_q}\}$:

$$\alpha_{l_1,1}r_{l_1} + \alpha_{l_2,1}r_{l_2} + \dots + \alpha_{l_q,1}r_{l_q} =$$

$$-\alpha_{h_1,1}r_{h_1} - \alpha_{h_2,1}r_{h_2} - \dots - \alpha_{h_{p-q},1}r_{h_{p-q}}$$

$$\alpha_{l_1,2}r_{l_1} + \alpha_{l_2,2}r_{l_2} + \dots + \alpha_{l_q,2}r_{l_q} =$$

$$-\alpha_{h_1,2}r_{h_1} - \alpha_{h_2,2}r_{h_2} - \dots - \alpha_{h_{p-q},2}r_{h_{p-q}}$$

$$\dots$$

$$\alpha_{l_1,q}r_{l_1} + \alpha_{l_2,q}r_{l_2} + \dots + \alpha_{l_q,q}r_{l_q} =$$

$$-\alpha_{h_1,q}r_{h_1} - \alpha_{h_2,q}r_{h_2} - \dots - \alpha_{h_{p-q},q}r_{h_{p-q}} \quad (43)$$

Substituting the solution of eq 43 into eq 15, after a few transformations based on the properties of the determinants, we obtain

$$P(r_{h_1}, r_{h_2}, \dots, r_{h_{p-q}}):$$

$$\frac{1}{\nu_1 \Delta} \sum_{k=1}^{p-q} \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_q,1} & \beta_{l_1,1} \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_q,2} & \beta_{l_2,1} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_q,q} & \beta_{l_q,1} \\ \alpha_{h_k,1} & \alpha_{h_k,2} & \dots & \alpha_{h_k,q} & \beta_{h_k,1} \end{vmatrix} r_{h_k} = r_{\text{OR}} \quad (44)$$

where the determinant

$$\Delta = \Delta(l_1, l_2, \dots, l_q) = \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_q,1} \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_q,2} \\ \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_q,q} \end{vmatrix} \quad (45)$$

Obviously, only those selections of the set of integers (l_1, l_2, \dots, l_q) are valid for which the determinant $\Delta = \Delta(l_1, l_2, \dots, l_q)$, eq 45, is different from zero. The TNs that correspond to these direct OR QSS conditions are denoted by $n_T(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q}})$, and their general connectivity is given by

$$n_T(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q}}):$$

$$\frac{1}{\nu_1 \Delta} \sum_{k=1}^{p-q} \begin{vmatrix} \alpha_{l_1,1} & \alpha_{l_2,1} & \dots & \alpha_{l_q,1} & \beta_{l_1,1} \\ \alpha_{l_1,2} & \alpha_{l_2,2} & \dots & \alpha_{l_q,2} & \beta_{l_2,1} \\ \dots & \dots & \dots & \dots & \dots \\ \alpha_{l_1,q} & \alpha_{l_2,q} & \dots & \alpha_{l_q,q} & \beta_{l_q,1} \\ \alpha_{h_k,1} & \alpha_{h_k,2} & \dots & \alpha_{h_k,q} & \beta_{h_k,1} \end{vmatrix} s_{h_k} + \text{OR} \quad (46)$$

Notice that in eq 46 the OR is added to the first term rather than subtracted as it would follow from eq 43. As shown below, this change in sign is dictated by the necessity to ensure that the RR graphs are cyclic graphs. It should also be noted that, in deriving eqs 44 and 45, we have arbitrarily utilized the first identity in eq 15. It may be shown, however, that, up to a constant, the final result is independent of the choice of the identities in eq 15.

The complete enumeration of the TNs may be, in general, performed by applying eq 44 to all possible combinations of $\{r_{l_1}, r_{l_2}, \dots, r_{l_q}\}$ ($1 \leq l_1 < l_2 < \dots < l_q \leq p$) or $\{r_{h_1}, r_{h_2}, \dots, r_{h_{p-q}}\}$ ($1 \leq h_1 < h_2 < \dots < h_{p-q} \leq p$) for which the determinant Δ , eq 45, is different from zero.

The connectivity of INs and TNs, in principle, provides the necessary information for constructing the RR graph. Of course, not all INs and TNs are independent; only q INs (the number

of independent intermediate species) and one TN (for the single OR) are independent.

Minimal and Non-Minimal Reaction Route Graphs

We distinguish explicitly between two types of reaction mechanisms resulting from the properties of the direct FRs, ERs, INs, and TNs. Namely, a mechanism in which the stoichiometric numbers in any direct RR, either FR or ER, or the stoichiometric number of individual elementary reaction steps and ORs incident to or from any IN or TN are equal to ± 1 is called a *minimal* mechanism, and the resulting RR graph is minimal. If at least one stoichiometric number in a direct RR or the stoichiometric number of individual elementary reaction steps or ORs incident to or from at least one IN or TN is equal to ± 2 , ± 3 , and so forth, the mechanism is called *non-minimal*, and the resulting RR graph is non-minimal. In other words, a minimal RR graph is one in which all of the elementary reaction steps, as well as the OR, are involved only *once* in the graph and in every FR, ER, IN, and TN. In a non-minimal RR graph, an elementary reaction step or the OR may be involved in a direct FR, ER, IN, or TN *more* than once.

The occurrence of a given reaction step at more than one location in the RR graph has a profound effect on its topology by virtue of the fact that, regardless of location, the elementary step affinity A_ρ as well as the reaction rate r_ρ must remain unchanged. This requirement, as we shall see, imparts symmetry to the RR graph, including the occurrence of *each* branch twice, for example.

We are now in a position to generalize the concept of a RR graph. Thus, a minimal or non-minimal RR graph is a cyclic digraph G_R satisfying the following conditions:

- The branches in a G_R individually represent the elementary reaction steps s_ρ ($\rho = 1, 2, \dots, p$) from the reaction mechanism, as well as the overall reaction OR.
- The nodes in a G_R are either INs, that is, $n_I(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q+1}})$ or TNs, that is, $n_T(s_{h_1}, s_{h_2}, \dots, s_{h_{p-q}})$.
- The cycles in a G_R are ERs.
- Any path in a G_R between two INs is an IR.
- Any path in a G_R between two TNs is a FR.
- The RR graph G_R includes, as paths, the complete list of direct FRs and ERs enumerated by other means.

It was mentioned above that a given reaction step may occur more than once in a RR graph having a profound effect on the topology of the RR graphs. To better understand the topological properties of the RR graphs, it is useful to extend the concept of directness of the RRs to RR graphs. Namely, we define a *direct* RR graph (not to be confused with *directed* graphs) as a RR graph in which all of the resulting FRs are direct. A *non-direct* RR graph is one that involves a complete set of direct FRs and, *additionally*, at least one non-direct FR. On the basis of these definitions, a key difference between a minimal and non-minimal RR graph may be formulated as the following: a minimal RR graph is always a direct RR graph, while a non-minimal RR graph may be either direct or non-direct.

The concept of directness of the RR graphs is an important tool in analyzing and rationalizing the efficacy of the reaction mechanism. More specifically, a mechanism that may be described by a direct RR graph is expected to be more efficient in producing the OR. In other words, such a mechanism produces the OR only via the shortest (direct) FRs, or alternatively, the FRs in direct RR graphs are free of ERs. On the contrary, a mechanism that is described by a non-direct RR graph is expected to be less effective in producing the OR. In other words, such mechanisms produce the OR not only via

the shortest (direct) FRs but also through long (non-direct) FRs. As a consequence, non-direct RR graphs are topologically less effective in the production of the OR.

Construction of Non-Minimal RR Graphs

The methods described previously to construct minimal RR graphs¹² cannot be utilized directly for constructing non-minimal RR graphs. In particular, the application of an incidence matrix is problematic since, in a non-minimal RR graph, a given elementary reaction step that is involved more than once may be in different locations of the graph. Two qualitative algorithms for the construction of a non-minimal RR graph are formulated here. Other algorithms are, of course, possible.

The starting point is the complete set of direct FRs, ERs, INs, and TNs that can be enumerated via the methodology described above. Next, the elementary reaction steps comprising a given IN are graphically depicted as directed branches around its *central node* according to their number and direction (sign). The elementary reaction steps comprising the IN are further interconnected so as to satisfy the shortest direct ERs. This will result in a graphical construction referred to as a RR *sub-graph* and denoted by G_n where the subscript “ n ” refers to a particular IN. The RR sub-graph G_n involves a *central node*, which is necessarily *balanced* in that it satisfies the connectivity as well as the intermediate QSS conditions, along with a set of *peripheral nodes*. Although in some particular cases it may happen that some peripheral nodes in G_n are also balanced, in general, the peripheral nodes in a RR sub-graph are *unbalanced*, i.e., they do not satisfy the connectivity dictated by the intermediate or the OR QSS conditions. This procedure may be continued, i.e., each of the peripheral nodes is transformed into either a balanced IN or TN resulting in the final RR graph. A properly balanced RR graph should also necessarily incorporate the complete list of enumerated direct FRs and ERs, i.e., a RR graph should involve at least two TNs and an OR which should produce the complete list of the direct FRs.

In the particular case of reaction mechanisms in which the stoichiometric number of elementary reaction steps and ORs in every FR, ER, IN, and TN does not exceed ± 2 , we have noticed that, as a consequence of the invariance of r_ρ and A_ρ , the RR graph is symmetrical and involves each elementary reaction step and OR exactly twice. Therefore, for this particular case, the construction algorithm may be simplified in analogy with the algorithm described previously in connection with minimal RR graphs.¹² Namely, start with a set of $p - q$ linearly independent RRs comprising one of the shortest minimal FRs, the remaining $p - q - 1$ being the smallest ERs. Draw the FR along with another variation in which the order, but not the direction, of the elementary reaction steps is reversed. From a kinetic viewpoint, of course, the order of sequential steps is immaterial, although it is usually significant mechanistically. Next, begin placing the ERs, simultaneously, in both sub-graphs, starting with the shortest, such that none of the reaction steps is involved more than once in each of the sub-graphs. The two sub-graphs are next connected by fusing selected nodes only when the ERs cannot be contained entirely within each of the sub-graphs. Two nodes are said to be fused when they are replaced by a single node containing all branches incident on the original nodes.²⁰ If all of the shortest ERs have been placed, it remains only to balance the remaining nodes by attaching the OR according to an appropriate TN from the complete list of TNs. Finally, the resulting RR graph should be verified to ensure that all enumerated direct FR and ERs are depicted as paths. This also provides the number of branches B and the

TABLE 1: A Generalized Mechanism and the Overall Reaction of the Electrochemical Hydrogen Oxidation (S = Surface Site)

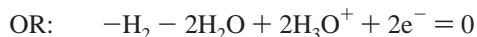
s_1 :	$H_2 + S \rightleftharpoons H_2 \cdot S$	
s_2 :	$H_2 \cdot S + S \rightleftharpoons 2H \cdot S$	
s_3 :	$H_2 + 2S \rightleftharpoons 2H \cdot S$	Tafel
s_4 :	$H_2O + H \cdot S \rightleftharpoons S + H_3O^+ + e^-$	Volmer
s_5 :	$H_2O + H_2 \cdot S \rightleftharpoons H \cdot S + H_3O^+ + e^-$	
s_6 :	$H_2O + H_2 + S \rightleftharpoons H \cdot S + H_3O^+ + e^-$	Heyrovski
OR:	$H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e^-$	

number of nodes N in a non-minimal graph. Thus, $B = 2(p + 1)$ and $N = 2(q + 2) - x$, where x is the number of fused nodes.

Examples

The theoretical developments described above are next illustrated with the help of three examples from different areas where this approach would be useful, namely, (1) electrochemistry, (2) atmospheric chemistry, and (3) gas-phase combustion. The examples were chosen so as to illustrate the main topological features of non-minimal, direct, and non-direct RR graphs.

Electrochemical Oxidation of Hydrogen. As the first example, we consider a modified version of the electrochemical hydrogen oxidation reaction (HOR) mechanism presented in Table 1. As can be seen, besides the conventional elementary reaction steps normally considered in the literature for the HOR, namely, the Tafel (s_3), the Volmer (s_4), and the Heyrovsky (s_6) steps,²¹ we assume that adsorbed molecular hydrogen may also exist as a distinct species (s_1), thus, resulting in an additional path for the formation of adsorbed atomic hydrogen (s_2) as well as a direct electrochemical oxidation path of the adsorbed molecular hydrogen (s_5). There is a single OR corresponding to the mechanism:



The stoichiometric matrix is

$$\nu = \begin{bmatrix} H_2 \cdot S & H \cdot S & S & H_2 & H_2O & H_3O^+ & e^- \\ +1 & 0 & -1 & -1 & 0 & 0 & 0 \\ -1 & +2 & -1 & 0 & 0 & 0 & 0 \\ 0 & +2 & -2 & -1 & 0 & 0 & 0 \\ 0 & -1 & +1 & 0 & -1 & +1 & +1 \\ -1 & +1 & 0 & 0 & -1 & +1 & +1 \\ 0 & +1 & -1 & -1 & -1 & +1 & +1 \end{bmatrix} \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix}$$

Hence, the system comprises $p = 6$ elementary reaction steps, $q = 2$ linearly independent intermediates (say, $H \cdot S$ and $H_2 \cdot S$), by virtue of the site balance, and $n = 4$ terminal species (H_2 , H_2O , H_3O^+ , and e^-). From the stoichiometric matrix, we select the intermediate submatrix α ,

$$\alpha = \begin{bmatrix} H_2 \cdot S & H \cdot S \\ +1 & 0 \\ -1 & +2 \\ 0 & +2 \\ 0 & -1 \\ -1 & +1 \\ 0 & +1 \end{bmatrix} \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix}$$

TABLE 2: A Complete List of Stoichiometrically Distinct Direct Full Routes (FRs), Empty Routes (ERs), Intermediate Nodes (INs), and Terminal Nodes (TNs) for the Electrochemical Hydrogen Oxidation

Full Routes	
FR ₁ : $s_1 + s_2 + 2s_4 = \text{OR}$	FR ₆ : $-s_3 + 2s_6 = \text{OR}$
FR ₂ : $s_1 - s_2 + 2s_5 = \text{OR}$	FR ₇ : $s_1 + s_4 + s_5 = \text{OR}$
FR ₃ : $-s_1 - s_2 + 2s_6 = \text{OR}$	FR ₈ : $s_4 + s_6 = \text{OR}$
FR ₄ : $s_3 + 2s_4 = \text{OR}$	FR ₉ : $2s_2 - s_3 - 2s_5 = \text{OR}$
FR ₅ : $2s_1 - s_3 + 2s_5 = \text{OR}$	FR ₁₀ : $-s_2 + s_5 + s_6 = \text{OR}$
Empty Routes	
ER ₁ : $s_1 + s_2 - s_3 = 0$	ER ₅ : $s_1 + s_2 + s_4 - s_6 = 0$
ER ₂ : $s_2 + s_4 - s_5 = 0$	ER ₆ : $s_1 - s_3 - s_4 + s_5 = 0$
ER ₃ : $s_1 + s_5 - s_6 = 0$	ER ₇ : $s_2 - s_3 - s_5 + s_6 = 0$
ER ₄ : $s_3 + s_4 - s_6 = 0$	
Intermediate Nodes	
n_{11} : $s_1 - s_2 - s_5$	n_{13} : $s_1 + s_2 + 2s_3 - s_4 + s_6$
n_{12} : $2s_2 + 2s_3 - s_4 + s_5 + s_6$	n_{14} : $2s_1 + 2s_3 - s_4 - s_5 + s_6$
Terminal Nodes	
n_{T1} : $\frac{1}{2}(s_4 + s_5 + s_6) + \text{OR}$	n_{T4} : $s_1 + s_3 + s_6 + \text{OR}$
n_{T2} : $s_2 + s_3 + s_5 + s_6 + \text{OR}$	n_{T5} : $-s_1 - s_3 + s_4 + s_5 + \text{OR}$
n_{T3} : $-s_2 - s_3 + s_4 + \text{OR}$	n_{T6} : $\frac{1}{2}(s_1 - s_2 + s_4 + s_6) + \text{OR}$

and a reduced stoichiometric submatrix γ , eq 7, with the rank equal to 3,

$$\gamma = \begin{bmatrix} H_2 \cdot S & H \cdot S & H_2 \\ +1 & 0 & -1 \\ -1 & +2 & -0 \\ 0 & +2 & -1 \\ 0 & -1 & 0 \\ -1 & +1 & 0 \\ 0 & +1 & -1 \end{bmatrix} \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix}$$

Our starting point in the construction of the RR graph is a set of direct FRs, ERs, INs, and TNs. These are enumerated using the above formalism.

a. Enumeration of the Direct FRs. The direct FRs are enumerated based on the intermediate matrix α . By definition, a direct FR in this system involves no more than rank $\alpha + 1 = 2 + 1 = 3$ linearly independent elementary reaction steps. Thus, any three linearly independent elementary reaction steps define a direct FR. For instance, elementary reaction steps s_1 , s_2 , and s_4 are linearly independent and, according to eq 28, define the following direct FR:

$$\text{FR}(s_1, s_2, s_4): \begin{vmatrix} +1 & 0 & s_1 \\ -1 & +2 & s_2 \\ 0 & -1 & s_4 \end{vmatrix} = s_1 + s_2 + 2s_4 = \text{OR}$$

A complete list of FRs may, thus, be generated by repeating this procedure over all possible selections of three linearly independent elementary reaction steps from a total of six. Thus, the number of direct FRs for this system does not exceed $(6!/3!)/3! = 20$. As can be seen from Table 2, only 10 of them, however, are distinct. Further, only $p - q = 6 - 2 = 4$ of these are independent.

b. Enumeration of the Direct ERs. The starting point in the enumeration of the direct ERs is the reduced stoichiometric matrix γ . By definition, a direct ER involves no more than rank $\gamma + 1 = q + 2 = 2 + 2 = 4$ elementary reaction steps define a direct ER. For instance, according to eq 33, the first four elementary reaction steps s_1 ,

s_2 , s_3 , and s_4 define the following direct ER:

ER(s_1, s_2, s_3, s_4):

$$\begin{vmatrix} +1 & 0 & -1 & s_1 \\ -1 & +2 & 0 & s_2 \\ 0 & +2 & -1 & s_3 \\ 0 & -1 & 0 & s_4 \end{vmatrix} = -s_1 - s_2 + s_3 = 0$$

Repeating this procedure over all combinations of four elementary reaction steps from the total of six results in $(6!/4!)/2! = 15$ possible direct ERs. However, only seven of these are stoichiometrically distinct (Table 2). Further, only $p - \text{rank } \nu = p - (q + 1) = 6 - 3 = 3$ of these are independent.

c. *Enumeration of the Direct INs.* The system includes two linearly independent intermediates, say, HS and H₂S. Thus, the intermediate QSS conditions may be presented as

$$Q_1: \quad r_1 - r_2 - r_5 = 0 \quad \text{H}_2\text{S}$$

$$Q_2: \quad 2r_2 + 2r_3 - r_4 + r_5 + r_6 = 0 \quad \text{H}\cdot\text{S}$$

Alternatively, these QSS conditions may be represented in terms of the intermediate matrix

$$\alpha^T = \begin{bmatrix} s_1 & s_2 & s_3 & s_4 & s_5 & s_6 \\ +1 & -1 & 0 & 0 & -1 & 0 \\ 0 & +2 & +2 & -1 & +1 & +1 \end{bmatrix} \begin{matrix} \text{H}\cdot\text{S} \\ \text{H}_2\text{S} \end{matrix}$$

By definition, a direct QSS condition may be obtained by linearly combining Q_1 and Q_2 so as to eliminate at least $q - 1 = 2 - 1 = 1$ rates. Alternatively, a direct QSS condition will involve no more than $p - (q - 1) = 6 - 2 + 1 = 5$ rates. For instance, if we choose to eliminate r_2 , the respective direct QSS condition will involve the remaining rates, that is, r_1, r_3, r_4, r_5 , and r_6 . According to eq 40, we have

$$Q(r_1, r_3, r_4, r_5, r_6): \quad \begin{vmatrix} -1 & Q_1 \\ +2 & Q_2 \end{vmatrix} = -(Q_1 + 2Q_2) = 0$$

which, thus, represents the QSS condition for the intermediate species $\text{H}_2\text{S} + 2\text{H}\cdot\text{S}$. Employing the equations for Q_1 and Q_2 , we have

$$Q(r_1, r_3, r_4, r_5, r_6): \quad 2r_1 + 2r_3 - r_4 - r_5 + r_6 = 0$$

The respective IN is

$$n_1(s_1, s_3, s_4, s_5, s_6): \quad 2s_1 + 2s_3 - s_4 - s_5 + s_6$$

A complete list of INs may be generated by repeating this procedure over the total number of possible selections of one rate from a total of six thus resulting into six possible INs. In reality, only four INs are distinct (Table 2). These INs were simply numbered from n_{11} to n_{14} . In fact, only $q = 2$ of these are independent.

d. *Enumeration of the Direct TNs.* The conventional OR QSS conditions may be expressed in terms of any terminal species. For instance, selecting the terminal species H_2 gives the following OR QSS conditions:

$$r_{\text{OR}} = r_1 + r_3 + r_6$$

Now, we can substitute any two of these rates with the remaining rates using the conventional intermediate QSS conditions, i.e., Q_1 and Q_2 . In doing this, we can employ eq 45. For instance,

eliminating r_1 and r_3 will result in a direct OR QSS condition involving r_2, r_4, r_5 , and r_6 . The determinant formed from the intermediate matrix α corresponding to r_1 and r_3 , eq 45, is different from zero:

$$\Delta(1, 3) = \begin{vmatrix} +1 & 0 \\ 0 & +2 \end{vmatrix} = 2 \neq 0$$

Thus, r_1 and r_3 are an appropriate selection. According to eq 44, the resulting direct OR QSS condition is

$P(r_2, r_4, r_5, r_6)$:

$$-\frac{1}{2} \left\{ \begin{vmatrix} +1 & 0 & -1 \\ 0 & +2 & -1 \\ -1 & +2 & 0 \end{vmatrix} r_2 + \begin{vmatrix} +1 & 0 & -1 \\ 0 & +2 & -1 \\ 0 & -1 & 0 \end{vmatrix} r_4 + \begin{vmatrix} +1 & 0 & -1 \\ 0 & +2 & -1 \\ -1 & +1 & 0 \end{vmatrix} r_5 + \begin{vmatrix} +1 & 0 & -1 \\ 0 & +2 & -1 \\ 0 & +1 & -1 \end{vmatrix} r_6 \right\} = \frac{1}{2}(r_4 + r_5 + r_6)$$

The direct TN corresponding to this direct OR QSS condition is

$$n_T(s_2, s_4, s_5, s_6): \quad \frac{1}{2}(s_4 + s_5 + s_6) + \text{OR}$$

Repeating this procedure over all choices of two rates from a total of six rates gives the complete set of direct OR QSS conditions. The stoichiometrically distinct direct TNs corresponding to these OR QSS conditions are presented in Table 2.

e. *Construction of the RR Graph.* Once all the FRs, ERs, INs, and TNs have, thus, been enumerated, we may proceed to construct the RR graph. According to the algorithm described above, the first step is the construction of the RR sub-graphs G_n . The procedure is illustrated in Figure 1 for all four INs. Thus, the elementary reaction steps involved in the INs are connected to the central node according to their occurrence and direction (sign). Next, we employ the list of direct ERs, Table 2, to interconnect in all possible ways the elementary reaction steps incident to or from the central node. In doing this, we use only the shortest ERs, that is, the three-membered ERs. From Figure 1, it is seen that three out of five peripheral nodes in the RR sub-graph G_3 are balanced INs, while the remaining two peripheral nodes may be transformed into balanced TNs by attaching the OR. According to the list of TNs, Table 2, the two peripheral nodes in G_3 may be transformed into TNs employing the OR QSS condition in the form $r_{\text{OR}} = 1/2(r_4 + r_5 + r_6)$ or, equivalently, $s_4 + s_5 + s_6 + 2\text{OR}$. Hence, the TNs should involve the OR twice. The resulting RR graph is shown in Figure 2.

On the other hand, although all of the peripheral nodes in G_1 may be balanced into TNs, the resulting graph is not a RR graph; that is, it does not produce an OR. Hence, at least two peripheral nodes in G_1 should be further rebalanced into INs. Similarly, the peripheral nodes in the RR sub-graphs G_2 and G_4 need to be further balanced in order to transform them into RR graphs. Because of complexity, further enumeration of these is not considered here. G_3 is a satisfactory direct RR graph for this non-minimal mechanism, i.e., it involves only direct FRs.

The second algorithm discussed above to construct the RR graph is illustrated in Figure 3. Here, the starting point is a set

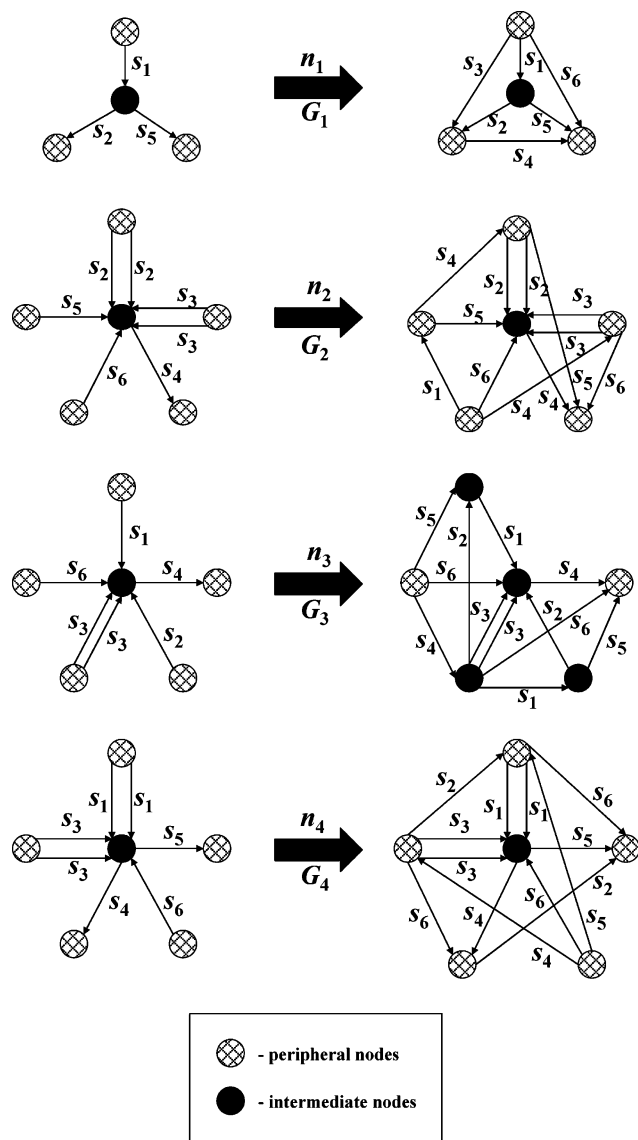


Figure 1. The transformation of the intermediate nodes into RR sub-graphs.

of linearly independent RRs comprising a single shortest minimal FR and the remaining shortest ERs. As can be seen from Table 2, these are

$$\text{FR}_8: s_4 + s_6 = \text{OR}$$

$$\text{ER}_1: s_1 + s_2 - s_3 = 0$$

$$\text{ER}_2: s_2 + s_4 - s_5 = 0$$

$$\text{ER}_3: s_1 + s_5 - s_6 = 0$$

We start with the two sub-graphs comprising only the FR with the order of elementary reaction steps in one of them reversed. In the next step (a), ER_2 is appropriately placed on both sub-graphs. It is further observed that there is no way to place in each sub-graph another ER without involving a reaction step more than once. Therefore, in the next step (b), ER_1 and ER_3 are placed such that the two sub-graphs become connected. After this stage, it is seen that all the nodes, except two, are balanced INs. The unbalanced nodes may be further balanced by fusing and transforming them into the terminal nodes n_{T1} and $-n_{\text{T1}}$ (step c).

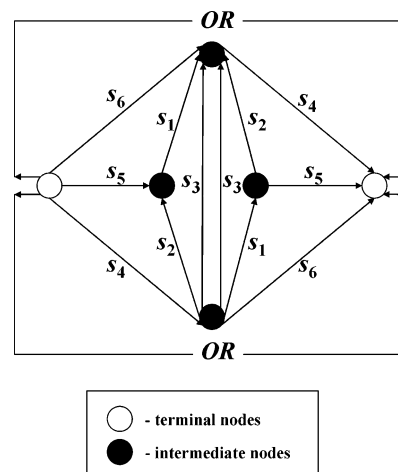


Figure 2. RR graph for the electrochemical hydrogen oxidation reaction.

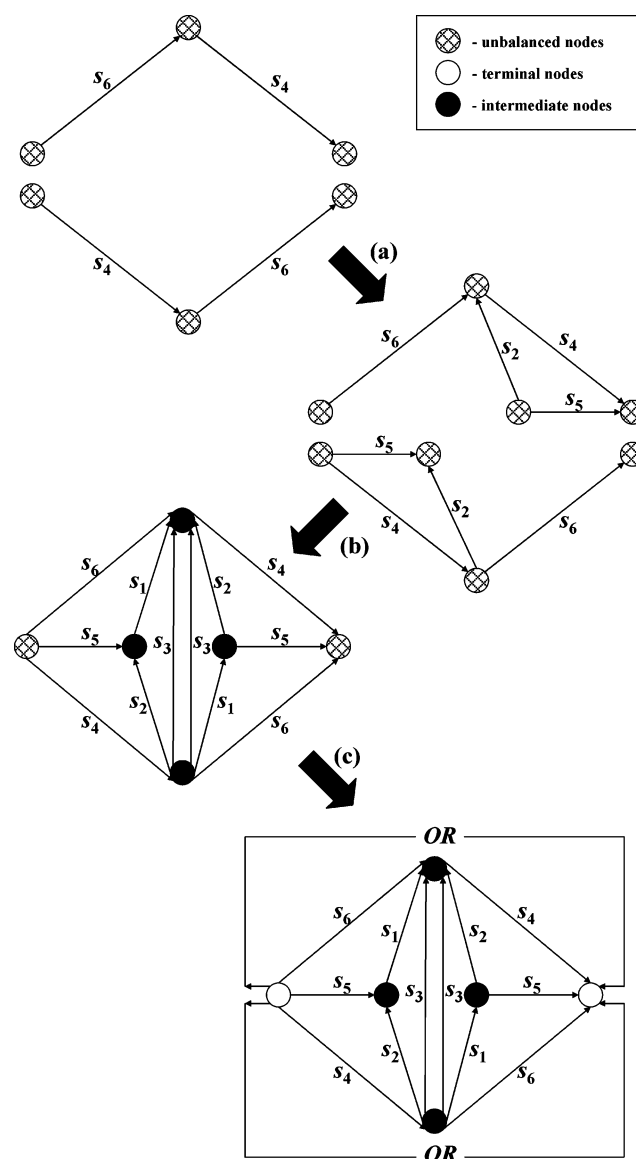


Figure 3. Construction of the RR graph for the electrochemical hydrogen oxidation reaction.

By inspection, it is seen that the resulting RR graph is direct and incorporates every branch twice, including the OR. The RR graph is also symmetric.

Ozone Destruction Reaction. As a second example, we consider a simplified version of the mechanism of ozone destruction via hydrogen oxide radicals (HO_x) in the middle atmosphere, although the destruction of photochemically generated Cl or Br atoms from CFCs and CH_3Br in the stratosphere is more important.²² The list of elementary reaction steps, including the overall reaction, is presented in Table 3. From these, we deduce the following stoichiometric matrix:

$$\nu = \begin{array}{ccccc} & \text{H} & \text{OH} & \text{HO}_2 & \text{O} & \text{O}_2 & \text{O}_3 \\ \begin{bmatrix} +1 & -1 & 0 & -1 & +1 & 0 \\ -1 & 0 & +1 & 0 & -1 & 0 \\ 0 & +1 & -1 & -1 & +1 & 0 \\ -1 & +1 & 0 & 0 & +1 & -1 \\ 0 & -1 & +1 & 0 & +1 & -1 \\ 0 & +1 & -1 & 0 & +2 & -1 \end{bmatrix} & \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix} \end{array}$$

The system comprises four intermediates, namely, H, OH, HO_2 , and O, as well as two terminal species, that is, O_2 and O_3 . Only three intermediates out of four, however, are linearly independent by virtue of mass balance. Indeed, the hydrogen mass balance requires

$$\begin{bmatrix} +1 \\ -1 \\ 0 \\ -1 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} -1 \\ 0 \\ +1 \\ +1 \\ -1 \\ +1 \end{bmatrix} + \begin{bmatrix} 0 \\ +1 \\ -1 \\ 0 \\ +1 \\ -1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

Hence, one of the intermediates, say, HO_2 , may be dropped, thus, resulting into the following intermediate submatrix:

$$\alpha = \begin{array}{ccccc} & \text{H} & \text{OH} & \text{O} & \\ \begin{bmatrix} +1 & -1 & -1 \\ -1 & 0 & 0 \\ 0 & +1 & -1 \\ -1 & +1 & -1 \\ 0 & -1 & 0 \\ 0 & -1 & 0 \end{bmatrix} & \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix} \end{array}$$

Similarly, we define a reduced stoichiometric matrix γ , eq 7,

$$\gamma = \begin{array}{ccccc} & \text{H} & \text{OH} & \text{O} & \text{O}_2 \\ \begin{bmatrix} +1 & -1 & -1 & +1 \\ -1 & 0 & 0 & -1 \\ 0 & +1 & -1 & +1 \\ -1 & +1 & -1 & +1 \\ 0 & -1 & 0 & +1 \\ 0 & -1 & 0 & +2 \end{bmatrix} & \begin{matrix} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \end{matrix} \end{array}$$

From these matrices, a complete list of FRs, ERs, INs, and TNs may be generated as described above and illustrated in the hydrogen electrochemical oxidation reaction example. For brevity, these calculations are not presented here, but their results are summarized in Table 4. Further, only the second algorithm is used to draw the graph.

TABLE 3: A Simplified Mechanism and the Overall Reaction of the Ozone Destruction in the Middle Atmosphere

s_1 :	$\text{OH} + \text{O} \rightleftharpoons \text{H} + \text{O}_2$
s_2 :	$\text{H} + \text{O}_2 \rightleftharpoons \text{HO}_2$
s_3 :	$\text{HO}_2 + \text{O} \rightleftharpoons \text{OH} + \text{O}_2$
s_4 :	$\text{H} + \text{O}_3 \rightleftharpoons \text{OH} + \text{O}_2$
s_5 :	$\text{OH} + \text{O}_3 \rightleftharpoons \text{HO}_2 + \text{O}_2$
s_6 :	$\text{HO}_2 + \text{O}_3 + \text{OH} + 2\text{O}_2$
OR:	$2\text{O}_3 \rightleftharpoons 3\text{O}_2$

TABLE 4: A Complete List of Stoichiometrically Distinct Direct Full Routes (FRs), Empty Routes (ERs), Intermediate Nodes (INs), and Terminal Nodes (TNs) for Ozone Destruction

Full Routes	
FR ₁ : $s_1 - s_2 - s_3 + 2s_4 = \text{OR}$	FR ₄ : $-s_2 + s_4 + s_5 = \text{OR}$
FR ₂ : $-s_1 - s_2 + s_3 + 2s_5 = \text{OR}$	FR ₅ : $s_5 + s_6 = \text{OR}$
FR ₃ : $s_1 + s_2 - s_3 + 2s_6 = \text{OR}$	FR ₆ : $s_1 - s_3 + s_4 + s_6 = \text{OR}$
Empty Routes	
ER ₁ : $-s_1 + s_3 - s_4 + s_5 = 0$	ER ₃ : $s_1 + s_2 - s_3 - s_5 + s_6 = 0$
ER ₂ : $s_2 - s_4 + s_6 = 0$	
Intermediate Nodes	
n_{11} : $-2s_1 + s_4 - s_5 + s_6$	n_{14} : $s_1 + s_3$
n_{12} : $-s_2 + s_3 - s_5 + s_6$	n_{15} : $-s_1 - s_2 - s_5 + s_6$
n_{13} : $-2s_1 + s_2 - s_3 + s_4$	n_{16} : $-s_1 + s_2 + s_4$
Terminal Nodes	
n_{T1} : $s_4 + s_5 + s_6 + 2\text{OR}$	n_{T5} : $s_2 + s_4 + s_5 + \text{OR}$
n_{T2} : $-s_3 + s_5 + \text{OR}$	n_{T6} : $s_1 + s_5 + \text{OR}$
n_{T3} : $s_3 + s_4 + s_6 + \text{OR}$	n_{T7} : $-s_1 + s_4 + s_6 + \text{OR}$
n_{T4} : $-s_2 + s_6 + \text{OR}$	

Our starting point in the construction of the RR graph is a set of $p - q = 3$ linearly independent RRs comprising a single shortest FR, the remaining two being the shortest ERs, that is,

$$\text{FR}_5: s_5 + s_6 = \text{OR}$$

$$\text{ER}_1: -s_1 + s_3 - s_4 + s_5 = 0$$

$$\text{ER}_2: s_2 - s_4 + s_6 = 0$$

The construction of the RR graph following the simplified algorithm described above is illustrated in Figure 4, and the steps involved are self-evident. By inspection, it can be verified that the resulting RR graph is a direct RR graph, that is, involves only direct FRs. Again, it should be noticed that the RR graph is symmetrical and involves every elementary reaction step twice.

Hydrogen Combustion Reaction. As a third example illustrating the concept of non-minimal, non-direct RR graphs, we consider the reduced seven elementary reaction step, one OR mechanism (Table 5), describing the gas-phase hydrogen

TABLE 5: A Simplified Mechanism and the Overall Reaction of the Gas-Phase Hydrogen Oxidation Reaction

s_1 :	$\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}$
s_2 :	$\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$
s_3 :	$\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2 + \text{O}_2$
s_4 :	$\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$
s_5 :	$\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$
s_6 :	$\text{H} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{OH}$
s_7 :	$\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$
OR:	$2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$

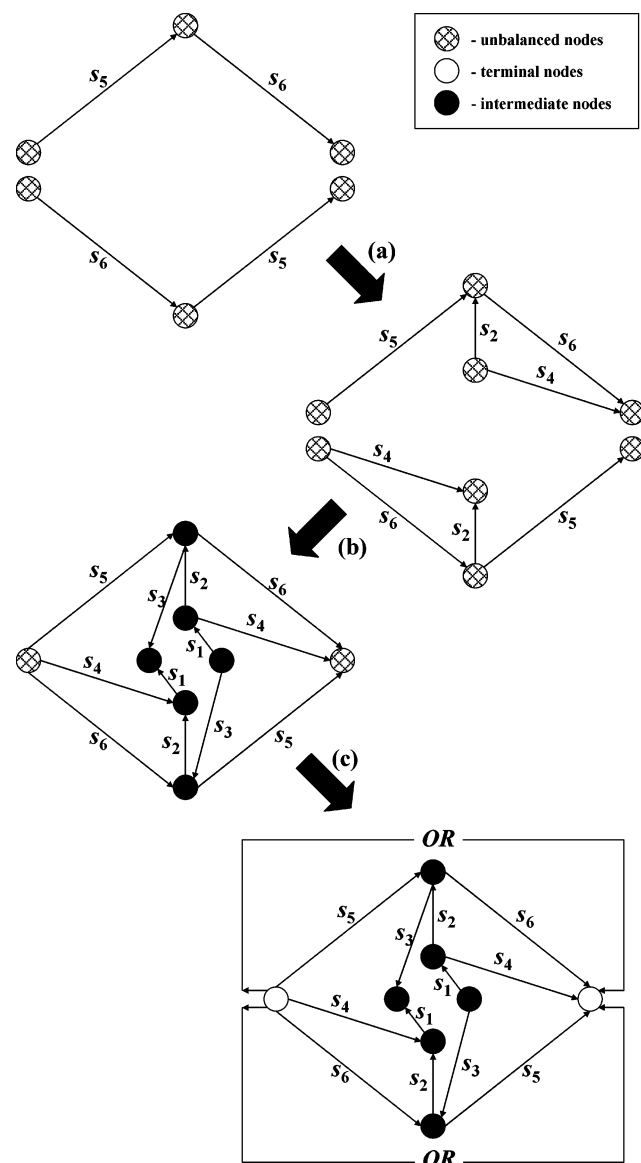


Figure 4. Construction of the RR graph for ozone destruction reaction.

oxidation reaction.²³ Although the full mechanism includes about 20 elementary reaction steps, the seven elementary reaction steps assumed here are considered to be the most important ones. In particular, they are the core reaction steps in any reduced mechanism.²³

The stoichiometric matrix for this system is

$$\nu = \begin{array}{c} \begin{array}{ccccccc} \text{H} & \text{O} & \text{OH} & \text{HO}_2 & \text{H}_2 & \text{O}_2 & \text{H}_2\text{O} \end{array} \\ \begin{array}{ccccccc} \left[\begin{array}{ccccccc} +1 & 0 & -1 & 0 & -1 & 0 & +1 \\ +1 & -1 & +1 & 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & -1 & +1 & +1 & 0 \\ -1 & +2 & +2 & 0 & 0 & -1 & 0 \\ -1 & 0 & 0 & +1 & 0 & -1 & 0 \\ -1 & 0 & +2 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 0 & +1 & +1 \end{array} \right] \end{array} \begin{array}{l} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \\ s_7 \end{array} \end{array}$$

As can be seen, the system comprises $p = 7$ elementary reaction steps, $l = 4$ intermediates H, O, OH, and HO_2 , and $n = 3$ terminal species H_2 , O_2 , and H_2O . The intermediates are linearly

TABLE 6: A Complete List of Stoichiometrically Distinct Direct Full Routes (FRs), Empty Routes (ERs), Intermediate Nodes (INs), and Terminal Nodes (TNs) for the Gas-Phase Hydrogen Oxidation Reaction

Full Routes	
FR ₁ : $2s_1 + s_2 + s_3 + s_4 + s_5 = \text{OR}$	FR ₄ : $s_2 - s_3 + s_4 + s_5 + 2s_7 = \text{OR}$
FR ₂ : $2s_1 + s_5 + s_6 = \text{OR}$	FR ₅ : $-2s_3 + s_5 + s_6 + 2s_7 = \text{OR}$
FR ₃ : $s_1 + s_2 + s_4 + s_5 + s_7 = \text{OR}$	FR ₆ : $2s_2 + 2s_4 + s_5 - s_6 + 2s_7 = \text{OR}$
Empty Routes	
ER ₁ : $s_1 + s_3 - s_7 = 0$	ER ₃ : $s_1 - s_2 - s_4 + s_6 - s_7 = 0$
ER ₂ : $s_2 + s_3 + s_4 - s_6 = 0$	
Intermediate Nodes	
n_{11} : $s_4 - s_5 + s_6$	n_{19} : $s_1 - s_3 - s_5 - s_6$
n_{12} : $s_3 - s_5 + s_6 + s_7$	n_{110} : $s_1 - s_3 - s_4 - 2s_6$
n_{13} : $s_3 - s_4 + s_7$	n_{111} : $s_1 - s_3 + s_4 - 2s_5$
n_{14} : $s_2 - s_4$	n_{112} : $s_1 - 2s_2 - 2s_6 + s_7$
n_{15} : $s_2 - s_3 - s_7$	n_{113} : $s_2 - s_5 + s_6$
n_{16} : $s_1 - 2s_5 + s_7$	n_{114} : $s_1 - s_2 - s_3 - 2s_6$
n_{17} : $s_1 - 2s_4 - 2s_6 + s_7$	n_{15} : $s_1 + s_2 - s_3 - 2s_5$
n_{18} : $s_1 - 2s_3 - 2s_6 - s_7$	
Terminal Nodes	
n_{T1} : $s_5 + \text{OR}$	n_{T5} : $s_1 + s_7 + 2\text{OR}$
n_{T2} : $s_4 + s_6 + \text{OR}$	n_{T6} : $s_1 - s_3 - s_6 + \text{OR}$
n_{T3} : $s_3 + s_6 + s_7 + \text{OR}$	n_{T7} : $s_1 - s_3 + s_4 + 2\text{OR}$
n_{T4} : $s_2 + s_6 + \text{OR}$	n_{T8} : $s_1 + s_2 - s_3 + 2\text{OR}$

independent, that is, $q = 4$, and hence, the reduced stoichiometric and intermediate matrices are

$$\gamma = \begin{array}{c} \begin{array}{ccccc} \text{H} & \text{O} & \text{OH} & \text{HO}_2 & \text{H}_2 \end{array} \\ \begin{array}{ccccc} \left[\begin{array}{ccccc} +1 & 0 & -1 & 0 & -1 \\ +1 & -1 & +1 & 0 & -1 \\ -1 & 0 & 0 & -1 & +1 \\ -1 & +2 & +2 & 0 & 0 \\ -1 & 0 & 0 & +1 & 0 \\ -1 & 0 & +2 & -1 & 0 \\ 0 & 0 & -1 & -1 & 0 \end{array} \right] \end{array} \begin{array}{l} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \\ s_7 \end{array} \end{array}$$

$$\alpha = \begin{array}{c} \begin{array}{ccccc} \text{H} & \text{O} & \text{OH} & \text{HO}_2 \end{array} \\ \begin{array}{ccccc} \left[\begin{array}{ccccc} +1 & 0 & -1 & 0 \\ +1 & -1 & +1 & 0 \\ -1 & 0 & 0 & -1 \\ -1 & +2 & +2 & 0 \\ -1 & 0 & 0 & +1 \\ -1 & 0 & +2 & -1 \\ 0 & 0 & -1 & -1 \end{array} \right] \end{array} \begin{array}{l} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \\ s_6 \\ s_7 \end{array} \end{array}$$

Employing these matrices, we can generate complete sets of direct FRs, ERs, INs, and TNs, and the results are summarized in Table 6.

The RR graph is constructed by employing the following set of $p - q = 3$ linearly independent RRs:

$$\text{FR}_3: s_1 + s_2 + s_4 + s_5 + s_7 = \text{OR}$$

$$\text{ER}_1: s_1 + s_3 - s_7 = 0$$

$$\text{ER}_2: s_2 + s_3 + s_4 - s_6 = 0$$

The construction procedure following the simplified algorithm is illustrated in Figure 5 and is self-explanatory. Upon inspection, it is seen that the resulting RR graph involves a complete set of direct FRs and ERs. At the same time, the RR graph

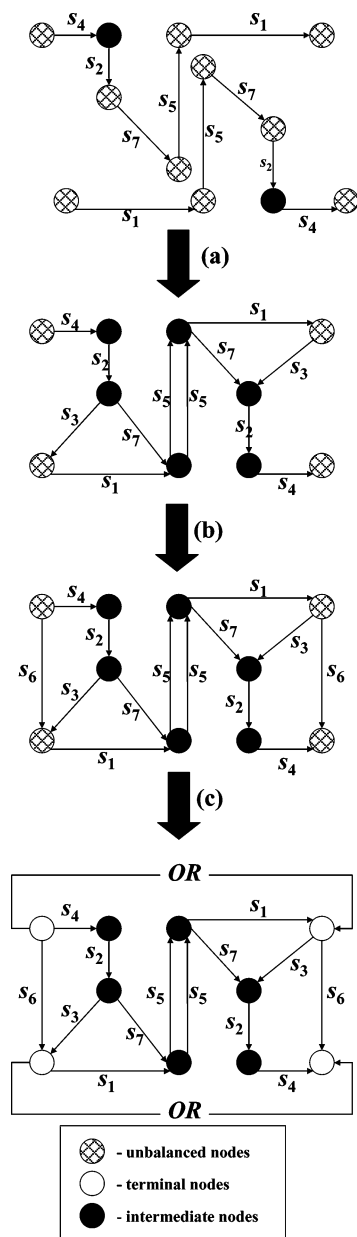


Figure 5. Construction of the RR graph for gas-phase hydrogen oxidation reaction.

involves two non-direct FRs. These are

$$\text{FR}_7: s_1 - s_3 + s_5 + s_6 + s_7 = \text{OR}$$

$$\text{FR}_8: s_1 + 2s_2 + s_3 + 2s_4 + s_5 - s_6 + s_7 = \text{OR}$$

Apparently, FR_7 is a direct FR since it involves no more than $q + 1 = 5$ elementary reaction steps. In reality, FR_7 is non-direct because it involves a cycle, that is, $\text{FR}_7 = \text{FR}_2 + \text{ER}_1$. Similarly, FR_8 also involves a cycle, that is, $\text{FR}_8 = \text{FR}_3 + \text{ER}_2$. Thus, the RR graph is non-direct.

Discussion and Concluding Remarks

In this work, we have addressed the problem concerning the topology of RR networks describing complex non-minimal reaction mechanisms. More specifically, we have shown that the concept of RR graphs developed by us for minimal reaction mechanisms (those with unit stoichiometric numbers) may be extended so as to treat more general non-minimal mechanisms (non-unit stoichiometric numbers). As shown previously, a

minimal RR graph is a unique topological structure that involves each reaction step only once and has a unique and finite number of direct FRs, ERs, INs, and TNs. In other words, when the terminology introduced in this work is employed, a minimal RR graph is always a direct RR graph.

In non-minimal RR graphs, however, reaction steps may occur more than once. As a consequence, non-minimal RR graphs may not necessarily be direct. That is, although non-minimal RR graphs still involve a complete set of direct RRs, they additionally may involve non-direct RRs. Thus, non-minimal RR graphs pose an interesting topological optimization problem, namely, how to generate RR graphs that are topologically the most effective in producing the OR.

Another major problem is that of simplification and reduction of the RR graphs employing the electrical circuit analogy; that is, the simplification and reduction procedures developed for minimal RR graphs should be substantially revisited. These and other related problems concerning non-minimal RR graphs are currently being investigated, and the results will be reported in due time.

On the symmetry of the resulting graphs for the examples considered in this work, we note that the requirement that the reaction affinity and rate must remain unchanged when a reaction step is placed at two different locations of the graph coupled with Kirchhoff's laws places certain limitations on the graph topology. For instance, it may be remarked that the resulting graphs in Figures 3–5 are symmetrical. Furthermore, each reaction step in each RR graph occurs exactly twice, including the OR. The simplification and reduction of the RR graphs employing the electrical circuit analogy will be considered in future work.

References and Notes

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