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Joseph D. Fehribach

Worcester Polytechnic Institute, bach@wpi.edu

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Vector-Space Methods and Kirchhoff Graphs for Reaction Networks

Joseph D. Fehribach
Fuel Cell Center
WPI Mathematical Sciences and Chemical Engineering
100 Institute Rd.
Worcester, MA 01609-2247

This article presents a vector space formulation for constructing reaction routes (reaction pathways) and Kirchhoff graphs (reaction route graphs) for reaction networks. Specific examples, many coming from fuel-cell electrochemistry, are included throughout to illustrate the more-general theoretical discussion.

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1 Introduction

For many years, reaction networks have been widely studied in the chemical and biological sciences, and a number of graphical approaches have been developed to help researchers understand these networks (cf. Fehribach [5] for an overview of these approaches). Among the most interesting of these are Kirchhoff graphs which allow a reaction network to be identified with a circuit diagram that satisfies the Kirchhoff laws. This article presents a mathematical, vector-space approach to understanding how Kirchhoff graphs correspond to reaction networks and most importantly, how to construct Kirchhoff graphs. These graphs have been defined and extensively discussed by Fishtik, et al. [10, 11, 12, 2, 6, 7, 9, 8, 13, 22] where they are termed “reaction route graphs.” The present author prefers the term “Kirchhoff graph” as it seems more general and more useful in helping the reader to understand what the key properties of these graphs are. The reaction networks that we consider come from fuel-cell electrochemistry, although the results presented here can be applied to any reaction network—chemical, biochemical or biological provided the network can be thought of as reversible.

For our purposes, assume that a reaction network is a collection of reacting chemical species (e.g., H₂, OH⁻, H₂O, CO₃⁻, etc.) and a set of reversible reaction steps (including irreversible reaction steps may be possible, but it would complicate the discussion, and so this issue will not be considered here). In Kirchhoff graphs, directed edges represent reaction steps, and vertices represent combinations of the reacting species—in particular their component potentials. Component potentials are the sums and differences of the electrochemical potentials for the reacting species weighted by the appropriate stoichiometric numbers. This implies that the potential difference between any two adjacent vertices is the affinity of the associated step. Indeed this potential difference must be the reaction step affinity no matter where the associated directed edge appears in the graph. The direction of each edge indicates the forward direction of the associated step. Vertices fall into two types: terminal vertices, corresponding to combinations of species which are either the products or the reactants for the overall reaction, and intermediate vertices, corresponding to combinations which contain (in part) intermediate species.

A Kirchhoff graph for a given reaction network must satisfy two fundamental defining properties:

• Every sequence of reaction steps which yields an overall reaction for the actual reaction network must have a corresponding sequence of edges which connect the terminal vertices associated with that overall reaction.

• The graph must satisfy Kirchhoff laws.

In saying the a Kirchhoff graph satisfies the Kirchhoff laws, one means that the graph satisfies the following four conditions:

• The sum of the reaction rates for the steps incident on each terminal vertex must be some stoichiometric multiple of the corresponding overall reaction rate.
• The sum of the reaction rates for steps incident on each intermediate vertex must be zero.

• The sum of the affinities (changes in potential) around any closed cycle must be zero.

• The sum of the affinities for any route (trail, path, walk) between two terminal vertices must be the affinity of the corresponding overall reaction.

The first two of these conditions are equivalent to the Kirchhoff current law; the last two are equivalent to the Kirchhoff potential law. One can then add edges representing the correct stoichiometric multiplicity of each overall reaction to make every Kirchhoff graph a cyclic graph.

Because Kirchhoff graphs satisfy the Kirchhoff laws, they allow one to study reaction networks using the tools that are traditionally used to study electrical circuits. Kirchhoff graphs and the associated systems of equations for the reaction rates and affinities of the individual reaction steps can be used to compute the overall rate and affinity for the reaction network. In addition, using the graph, one can determine which routes are most significant (offer the least resistance) and which can be eliminated as unnecessary because their rates are too small to be significant. Or the effects of, say, temperature on the reaction network can be considered since the rates of reaction steps vary independently with temperature. One can also define simpler equivalent Kirchhoff graphs which yield the same overall reactions and overall reaction rates. But the key point is that basic linear algebra guarantees that in a sense that will be made clear below, a Kirchhoff graph for a reaction network completely characterizes the reaction network. For a more-complete treatment of the applications of Kirchhoff (reaction route) graphs, see Fishtik et al. [2, 7, 9, 22].

Before one can use a Kirchhoff graph to study a reaction network, however, two basic questions should be considered: (1) does every reaction network have a corresponding Kirchhoff graph?, and (2) if there is a Kirchhoff graph, how can one construct it? The issue of existence will not be addressed in detail here, although the author conjectures that a Kirchhoff graph exists for any given reaction network. Assuming that a Kirchhoff graph does exist, we will consider two approaches for constructing it. In the first, one starts by constructing an auxiliary graph called an overall reaction graph. This construction is given in terms of vector space methods in the next section. The overall reaction graph can then act as a skeleton in the construction of a Kirchhoff graph. In a second more general approach, a Kirchhoff graph is obtained from the construction of an incidence matrix using row operations on the row space of the transpose of the stoichiometric matrix for the reaction network. This incidence-matrix approach is presented in Section 4 below.

The overall reaction(s) for a given reaction network may be known in advance, but as is discussed below, they are in general determined by the specific reacting species and reaction steps. The next section discusses the use of vector spaces in deciding which overall reactions are possible (achievable) for a given reaction network, then shows how linear algebra can be used to determine all sequences of reaction steps which yield an overall reaction by connecting the initial state representing the collection of reactant species to the final state representing the collection of product
species. These sequences are known in the literature as overall reaction routes, reaction pathways or reaction mechanisms. Having found all overall reaction routes, one can represent them graphically in terms of an overall reaction graph (mentioned above) which is a projection of the vector space construction just developed. Such an overall reaction graph satisfies the first defining property for a Kirchhoff graph (that it represents the overall reaction), and the Kirchhoff potential laws, but not necessarily the Kirchhoff current laws. It can thus be stepping stone in the construction of a Kirchhoff graph, and it implies that every Kirchhoff graph is in fact a geometric graph, i.e. it is based on an underlying vector space. Section 3 then discusses the construction of a Kirchhoff graph itself based on this overall reaction graph construction.

While Kirchhoff graphs have important implications for the study of reaction networks, they also have an inherent mathematical beauty and therefore are interesting in their own right. Kirchhoff graphs can be constructed for matrices in general, not just those coming from reaction stoichiometry. Finding a Kirchhoff graph is basically the inverse problem to the construction of the cycle space and bond space for a given graph [1]. In the concluding section, Section 5, some of the properties of the relationship between matrices and their associated Kirchhoff graphs are explored, independent of reaction networks. But a final example then makes clear how the study of a relatively complicated reaction network can be simplified and organized through an appropriate Kirchhoff graph.

As was mentioned above, reaction route graphs, which are essentially the same as Kirchhoff graphs, were defined by Fishtik, Datta et al. (2001-2007) [6, 7, 8, 22]. These authors contributed much to the understanding of this concept, particularly making clear its application to the study of the processes in reaction networks. Their approach for constructing the graphs, however, is based on a form of Cramer’s rule (cf. Appendix A, [11]) and is thus computationally inefficient. It also relies on lengthy lists or reaction routes and rate conditions, not taking advantage the concept of a vector space basis. Both of these issues are address in the present work.

Similar graphs have also been used by other authors. Horn (1973) [14, 15] proved a number of results about reaction diagrams and complex graphs which are similar to Kirchhoff graphs, though he considered reversible, weakly reversible and irreversible reactions. Feinberg et al. [20, 3, 4] have defined and studied species-complex-linkage graphs and species-reaction graphs which again are both similar to but distinct from the Kirchhoff graphs studied here. Oster, Perelson & Katchalsky (1973) [17] referred to Kirchhoff graphs as topological graphs. Also Roberts (1977) [19] used a form of Kirchhoff graph to help in his study of enzyme kinetics. More recently Qian, Beard & Liang (2003) [18] used a simple Kirchhoff graph in their study of a three-state kinetic cycle. None of these authors, however, considered the vector space aspects of Kirchhoff graphs, or studied the Kirchhoff graph concept in detail.

Finally, for readers less familiar with linear-algebraic concepts used here, a complete introduction to these concepts can be found in, e.g., Johnson & Riess [16] or Strang [21].
2 Vector Space Methods for Reaction Routes

Consider a reaction network composed of the following \( n \) reaction steps:

\[
0 \iff \alpha_{11}T_1 + \alpha_{12}T_2 + \ldots + \alpha_{1k}T_k + \beta_{11}I_1 + \beta_{12}I_2 + \ldots + \beta_{1\ell}I_\ell \\
0 \iff \alpha_{21}T_1 + \alpha_{22}T_2 + \ldots + \alpha_{2k}T_k + \beta_{21}I_1 + \beta_{22}I_2 + \ldots + \beta_{2\ell}I_\ell \\
\vdots \\
0 \iff \alpha_{n1}T_1 + \alpha_{n2}T_2 + \ldots + \alpha_{nk}T_k + \beta_{n1}I_1 + \beta_{n2}I_2 + \ldots + \beta_{n\ell}I_\ell
\]

(1)

Here \( T_j \) are the terminal species (species which are either produced or consumed by the reaction network, \( i.e. \), their net amounts change), and \( I_j \) are the intermediate species (species neither produced or consumed in the network). Even though they are not true intermediate species, reaction sites (often denoted S or M) are grouped with the intermediates when they appear in reaction steps because they are also not produced or consumed in any overall reaction. By convention, the stoichiometric coefficients (\( \alpha_{ij} \) and \( \beta_{ij} \)) are positive integers if the corresponding species is a product (produced by the \( i \)-th step), negative integers if it is a reactant (consumed in the \( i \)-th step), and zero if it is not present in the \( i \)-th step. This allows us to place all of the species on the right side of the chemical reaction equation.

Based on this reaction network, let us define vectors representing the reaction steps: \( s_i := [\alpha_{i1}, \alpha_{i2}, \ldots, \alpha_{ik}, \beta_{i1}, \beta_{i2}, \ldots, \beta_{i\ell}] \), and consider the vector space representing all linear combinations of the reaction steps: \( V := \text{span}\{s_1, s_2, \ldots, s_n\} \). Clearly \( V \) is a subspace of the entire stoichiometric coefficient space \( Q^{k+\ell} \) where \( Q \) represents the rational numbers. Since we are interested in determining overall reactions and finding routes that yield these overall reactions, let us divide \( Q^{k+\ell} \) into two subspaces: the first subspace associated with the terminal species can be identified with \( Q^k \), while the second associated with the intermediate species can be identified with \( Q^\ell \). For an overall reaction the stoichiometric coefficients for the intermediate species \( I_j \) must all be zero. So \( b \in Q^k \) is the vector representing an achievable overall reaction if and only if it can be written as a linear combination of the reaction step vectors \( s_i \) with only integer stoichiometric coefficients. Mathematically this means that \( b \in V \cap Q^k \), \( i.e. \) \( b \) must both be a linear combination of the \( s_i \) and have zero entries associated with the intermediate species. This arrangement is depicted in Figure 1.

In the remainder of this section, the most general full reaction route (combination of reaction steps) which results in a given overall reaction \( b \) will be derived. From a mathematically view, this amounts to a classical problem in linear algebra, and the result is well known. To accomplish our goal, we must first find all of the null or empty routes (equivalent to finding the homogeneous solution) then find which overall reactions are achievable, and finally combined the null routes with a full route (particular solution) to give a general representation of the full reaction route. The process for finding the full reaction route will be illustrated using the example of the hydrogen evolution reaction.
2.1 Null (Empty) Routes

The first key question that must be addressed is which routes lead nowhere, i.e., which linear combinations of reaction steps cancel themselves out leaving the amounts of all species unchanged. Such a route is shown in Figure 2. Notice that the vector graph corresponding to any null route is a cycle and that the coefficients $a_i$ must be integers. Let $A := [\alpha_{ij} | \beta_{ij}]^T$ be the transpose of the stoichiometric matrix, i.e., $A$ is the matrix whose $i$-th column contains the stoichiometric numbers from the $i$-th reaction. To find all possible null routes, one must find all possible solutions of $Av = 0$ which means that one must compute $\text{Null}(A)$, the null space of $A$. For convenience let $m$ be the dimension of $\text{Null}(A)$. Fortunately modern mathematical software such as MAPLE, MATHEMATICA or MATLAB make this computation relatively easy even when $k$, $\ell$, $m$ and $n$ are relatively large.

**Example 1a.** As a relatively simple example of this approach to finding reaction routes, consider the HER (Hydrogen Evolution Reaction) network. HER is important in, among other places, certain corrosion processes and its overall reaction (derived below) is well established. This network is composed of six species ($H_2$, $OH^-$, $H_2O$, $e^-$, $S$, $H\cdot S$) and three reaction steps. The first five species are the terminal species, the last ($H\cdot S$) is the only true intermediate species ($S$ is treated as an intermediate species for our purposes). The three reaction steps are

\[
\begin{align*}
  s_T : & \quad 2H\cdot S \rightleftharpoons 2S + H_2, \\
  s_V : & \quad S + H_2O + e^- \rightleftharpoons H\cdot S + OH^-, \\
  s_H : & \quad H\cdot S + H_2O + e^- \rightleftharpoons S + H_2 + OH^-.
\end{align*}
\]
Figure 2: Depiction of a null or empty route. Here the sum of $a_1s_1$, $a_3s_3$, $a_7s_7$ and $a_4s_4$, ends where it begins leaving the system unchanged.

The subscripts which distinguish the steps honor, respectively, Tafel, Volmer and Heyrovsky. Moving the reactants to the righthand side and giving them negative signs, one obtains the following stoichiometric table:

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>OH$^-$</th>
<th>H$_2$O</th>
<th>e$^-$</th>
<th>S</th>
<th>H·S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_T$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>$s_V$</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$s_H$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Based on this table, the stoichiometric matrix transpose is

$$A = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & -1 & -1 \\ 0 & -1 & -1 \\ 2 & -1 & 1 \\ -2 & 1 & -1 \end{bmatrix}. \quad (3)$$

By direct calculation, one finds that

$$\text{Null}(A) = \text{Span} \left\{ \begin{bmatrix} 1 \\ 1 \\ -1 \end{bmatrix} \right\} \quad (4)$$

which means that $s_T + s_V - s_H = 0$, i.e., that only multiples of this combination of steps leaves the system unchanged.
2.2 Overall Reactions

Once the null routes have been determined, the possible overall reaction(s) associated with our reaction network can be found. In some cases, these may be known in advance, but in general the overall reactions should be determined by the specific reaction steps and reacting species.

To determine what overall reactions are achievable, let \( B := [\beta_{ij}]^T = [\beta_{ji}] \) be the transpose of the matrix of stoichiometric coefficients for the \( n \) steps of our reaction network associated with just the reaction sites and the intermediate species. Because overall reactions must be both nontrivial and free of intermediate species, overall reactions correspond to the portion of \( \text{Null}(B) \) which is perpendicular to \( \text{Null}(A) \). Mathematically this relationship can be expressed as \( \text{Null}(B) = \text{Null}(A) \oplus OR \) where \( OR \) is the subspace corresponding to the overall reactions. The dimension of \( OR \) is the number of linearly independent overall reactions for our reaction network, and the overall reactions themselves can be determined from a basis for this subspace. Note that if \( \text{Null}(B) = \text{Null}(A) \), then \( OR \) is trivial and no overall reactions can be achieved. If \( OR \) is one dimensional, then there is a single basis vector and a single overall reaction. Because we are working with vector spaces over the rational numbers, it is possible to choose this basis vector to have integer entries with no common divisors (probably the simplest choice), keeping in mind that the entries for products should be positive, while those for reactants should be negative. If \( OR \) has dimension greater than one, then there are multiple overall reactions, and the situation is more complicated. In particular, if the null space is two dimensional, there are at least three distinct (though not linearly independent) overall reaction.

Example 1b. Now returning to the HER network, and considering only the intermediate species, one sees from Table 2.1 that the stoichiometric matrix for intermediate species is

\[
B = \begin{bmatrix}
2 & -1 & 1 \\
-2 & 1 & -1
\end{bmatrix}. \tag{5}
\]

Again by direct calculation, one finds that

\[
\text{Null}(B) = \text{Span} \left\{ \begin{bmatrix}
1 \\
1 \\
-1
\end{bmatrix}, \begin{bmatrix}
0 \\
1 \\
1
\end{bmatrix} \right\} \tag{6}
\]

Since the intersection of \( \text{Null}(A) \) and \( \text{Null}(B) \) is spanned by the vector \( [1, 1, -1]^T \), only the portion of the null space of \( B \) perpendicular to \( [1, 1, -1]^T \) represents a nontrivial overall reaction. Since the two basis vectors in (6) are perpendicular, \( OR = \text{Span}\{[0, 1, 1]^T\} \). Thus the overall reaction for the HER reaction network is the one corresponding to \( s_V + s_H \), which written in terms of species is the well-known overall reaction for the HER network:

\[
2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \]

Note that the above result guarantees that this is the only possible overall reaction for the HER reaction network.
2.3 Overall Reaction Routes

Now that the achievable overall reactions have been identified, let us consider what routes yield these overall reactions. Following Fishtik, et al. [11], for a given achievable overall reaction $b$, define an overall reaction route to be an integral linear combination of reaction steps which yields the overall reaction:

$$b = x_1 s_1 + x_2 s_2 + \ldots + x_n s_n$$  \hspace{1cm} (7)

where each $x_i$ is an integer. Let us consider in general how to find all the possible choices for $x_i$. The problem of finding overall reaction routes in fact simply amounts to finding the general solution of the system of linear equations

$$Ax = b$$  \hspace{1cm} (8)

where again $A$ be the transpose of the matrix of stoichiometric coefficients (the stoichiometric matrix). The well-known general solution of (8) is the sum of any particular solution $p$ and an element of the null space of $A$. Thus any overall reaction route associated with $b$ can be represented as a vector in the form

$$x = p + c_1 v_1 + c_2 v_2 + \ldots + c_m v_m$$  \hspace{1cm} (9)

where $p$ is our particular solution, $\{v_1, v_2, \ldots, v_m\}$ is a basis for Null($A$) (found in section 2.1 above) and the $c_i$ are arbitrary integers. Again finding a particular solution $p$ is greatly simplify through the use of MAPLE, MATHEMATICA or MATLAB. If the $s_i$ are in fact linearly independent, then this null space is trivial (contains only the zero vector), $m = 0$, there is only one particular solution, and the solution of (8) is unique: $x = p$, implying that there is only one reaction route that achieves the given overall reaction $b$. If, on the other hand, the $s_i$ are not linearly independent, then this null space contains nonzero vectors, and there are multiple overall reaction routes that achieve the overall reaction associated with $b$.

Example 1c. Returning once more to the HER example, Figure 3 shows two possible vector representations for the overall reaction routes for HER. Thus whilst all overall reaction routes $x$ are of the form given in (9), the graphical representation depends on the choice of $p$ and how the null cycle is adjoined to $p$, and therefore is not unique.

The graphs in Figure 3 are in fact both two-dimensional projections of the vector sum for $x$ given in (9), and directed graphs (digraphs) in the graph-theoretic sense. As such, they represent the connection between the vector-space development in this section and the Kirchhoff graphs of the next, and they give the starting point for constructing those Kirchhoff graphs.

2.4 Choosing a Basis for Null($A$)

Now suppose that the null space of $A$ is multi-dimensional ($m \geq 2$). Then the solution for (8) is not unique, and there are many possibilities for how to choose the basis vectors $v_i$ for Null($A$); what is the best choice? Although the answer to this
Figure 3: Two overall reaction graphs for the HER reaction network. In both versions, \( \text{Null}(A) \) is one dimensional and \( \mathbf{v}_1 \) corresponds to \( s_T + s_V - s_H = 0 \) is the sole basis vector for this null space. In the first version, \( \mathbf{p} \) corresponds to \( s_H + s_V \), while in the second, \( \mathbf{p} \) corresponds to \( s_T + 2s_V \). Based on the smallest total norm (defined below), the first version would be preferred.

The question depends on what one means by “best,” it is possible to see that there is a simplest choice in the following sense. Let

\[
||\mathbf{v}_i|| := \sum_{j=1}^{n} |v_{ij}|
\]  

(10)

be the norm (length) of \( \mathbf{v}_i \), and let

\[
TN := \sum_{i=1}^{m} ||\mathbf{v}_i||
\]  

(11)

be the total norm for the basis. We take as the best choice that which has a smallest total norm. Since the entries \( v_{ij} \) must be integers, a basis with minimal total norm must exist, although it might not be unique. In some cases finding exactly the best choice may not be necessary; a convenient basis with total norm that is not too large may be desirable for use in (9).

A similar minimal total norm criterion can also be used for determining a basis for the row space below, and for that matter for determining a “best” basis for any other finite vector space over the rationals.

So in summary, for a given reaction network, one can determine which overall reactions are achievable by finding all vectors \( \mathbf{b} \in \mathbb{Q}^k \) of the form given in (7). Then one can find all overall reaction routes associated with \( \mathbf{b} \) by finding a particular solution \( \mathbf{p} \) and a simple basis \( \{\mathbf{v}_1, \mathbf{v}_2, ..., \mathbf{v}_m\} \) for the null space of \( A \) and represent the overall reaction route as \( \mathbf{x} = \mathbf{p} + c_1\mathbf{v}_1 + c_2\mathbf{v}_2 + ... + c_m\mathbf{v}_m \).

3 Vector Spaces and Kirchhoff Graphs

The vector space methods used in the previous section to find reaction routes and overall reaction graphs can now be used to construct Kirchhoff graphs. As discussed
above, an overall reaction graph satisfies Kirchhoff’s potential laws; it is frequently possible to extend an overall reaction graph so that the extension also satisfies Kirchhoff’s current laws, \( i.e. \) that the rates associated with all reaction steps starting and ending at each vertex must sum to zero (once the overall reaction vectors have been included).

Figure 4: A planar Kirchhoff graph for the HER reaction network based on the overall reaction graphs in Figure 3. The central vertex is a null vertex.

As was the case for the potential laws in the previous section, the current laws here come directly from conditions on the intermediate and terminal species in the reaction network. In a reaction network, the rate at which intermediate species are produced and consumed must balance, meaning that there can be no net gain or loss in the network for any intermediate. For the terminal species, on the other hand, the rates of production and consumption are determined by the overall reaction rate. These conditions can be expressed in terms of an augmented version of the transpose of the stoichiometric matrix \( \mathbf{A} \). Suppose there are \( \mu \) linearly independent overall reactions. Let \( \tilde{\mathbf{A}} := \mathbf{A} | \mathbf{b}_1 | \mathbf{b}_2 | \ldots | \mathbf{b}_\mu \), \( i.e. \), the matrix \( \mathbf{A} \) with the overall reactions vectors \( \mathbf{b}_i \) adjoined to it. A Kirchhoff graph will then satisfy the current conditions if and only if the combinations of edges incident on each vertex of the graph lies in \( \text{Row}(\tilde{\mathbf{A}}) \), the row space of \( \tilde{\mathbf{A}} \). The meaning of this row-space requirement is best understood in terms of our HER example:

**Example 1d:** One last time, let us return to the HER reaction network. For this reaction network,

\[
\tilde{\mathbf{A}} = \begin{bmatrix}
1 & 0 & 1 & 1 \\
0 & 1 & 1 & 2 \\
0 & -1 & -1 & -2 \\
0 & -1 & -1 & -2 \\
2 & -1 & 1 & 0 \\
-2 & 1 & -1 & 0
\end{bmatrix}, \tag{12}
\]

So

\[
\text{Row}(\tilde{\mathbf{A}}) = \text{Span}\{\mathbf{w}_1, \mathbf{w}_2\}, \tag{13}
\]
where
\[
\begin{align*}
\mathbf{w}_1 &:= [1, 0, 1, 1], \\
\mathbf{w}_2 &:= [-1, 1, 0, 1] 
\end{align*}
\] (14)

satisfy the minimum norm requirement discussed above.

One now construct an HER Kirchhoff graph more-or-less by inspection. Since each of the overall reaction graphs in Figure 3 already satisfy the potential laws, either provides a starting point for constructing a Kirchhoff graph for HER. The goal is to check the existing vertices to see which satisfy the row space conditions, then create new null routes (cycles) by adding edges and vertices, including edges corresponding to overall reactions, to achieve a graph that does satisfy all the Kirchhoff conditions. Starting with the first version, notice that the vertex at the origin already satisfies a current condition (lies in the row space). The vertex at the top of the graph, on the other hand, does not lie in the row space, so one or more additional directed edges must be added to satisfy a current condition. The simplest way to do this is to add a copy of the overall reaction vector \( \mathbf{b} \) starting from the top vertex; then this top vertex does lie in the row space since it can be represented by \( \mathbf{w}_2 \).

Notice that adding this edge also creates a new vertex. From here, the simplest way to complete the process and achieve a Kirchhoff graph is to add two more edges: a copy of \( \mathbf{s}_T \) on the right side of the graph and a copy of \( \mathbf{s}_H \) heading from the center to the upper right hand vertex of the graph. The resulting Kirchhoff graph is shown in Figure 4. A simple check confirms that the resulting graph satisfies all the current and potential laws. Notice that the center vertex is a null vertex in the sense that \( \mathbf{s}_V \) and \( \mathbf{s}_H \) both head in and out. Such null vertices always lie in the row space (the zero vector must be in any vector space).

**Remarks.**

1. Because Kirchhoff graphs are geometric graphs (i.e., the edges of our Kirchhoff graphs are also projections of vectors in a vector space), the lengths and directions of all edges associated with a given reaction step are the same in Figure 4. So other versions of this Kirchhoff graph can be drawn by changing the angle of projection.

2. In some sense, the HER Kirchhoff graph in Figure 4 is the union of the two overall graphs in Figure 3. But not all Kirchhoff graphs can be easily constructed as the extension of a given overall reaction graph. In particular, Kirchhoff graphs are not unique. This can be seen when a Kirchhoff graph is a cycle since the order in which the edges appear around the cycle is arbitrary.

For a more interesting example, consider an alternate Kirchhoff graph for the HER network presented by Fishtik et al. [9] shown in Figure 5. Notice that this second Kirchhoff graph genuinely distinct, not just a different projection of the first: it has one less vertex than does the first and no null vertex. Which of these two Kirchhoff graphs one prefers depends on what use one wishes to make of the graph.
Figure 5: A second Kirchhoff graph for the HER reaction network. It is a Kirchhoff graph since it satisfies both the current and potential reaction conditions, but it is distinct from the previous Kirchhoff graph since it has a different number of vertices, and the vertices are associated with differing edges. In particular, this graph has no null vertex. It is a multigraph since multiple edges are needed to achieve the current balance at each of the vertices. Also, there is no planar representation for this graph because it must be a geometric graph.

4 Kirchhoff Graph from an Incidence Matrix

The previous section presented the construction of a Kirchhoff graph for a reaction network by inspection based on the overall reaction graph and the Kirchhoff current requirements. This approach works well when a Kirchhoff graph is close to the overall reaction graph, but it may not work well when the Kirchhoff graph is more complicated. The current section addresses this issue, presenting an approach which is based on the vector-space requirements, but not on the overall reaction graph construction. This discussion also makes clear that the Kirchhoff graph concept is in fact a property of a matrix whether or not the matrix is the transpose of the stoichiometric matrix of some reaction network.

Example 2a: Consider the following toy (model) reaction network made up of four intermediate species and four reaction steps:

\begin{align*}
s_1 : & \quad \text{CH}_4 + \text{C}_3\text{H}_8 \Rightarrow 2\text{C}_2\text{H}_6, \\
s_2 : & \quad 2\text{CH}_4 + \text{C}_4\text{H}_{10} \Rightarrow 3\text{C}_2\text{H}_6, \\
s_3 : & \quad \text{CH}_4 + 2\text{C}_4\text{H}_{10} \Rightarrow 3\text{C}_3\text{H}_8, \\
s_4 : & \quad \text{C}_2\text{H}_6 + \text{C}_4\text{H}_{10} \Rightarrow 2\text{C}_3\text{H}_8. \tag{15}
\end{align*}

This network has no terminal species and thus no overall reactions. Nonetheless, it demonstrates a nontrivial situation where the Kirchhoff graph is surprisingly com-

\footnote{This network was presented to the author by Ilie Fishtik as an example of a small but difficult network for which to construct a Kirchhoff or reaction route graph.}
plicated. Since there are no overall reactions, all the cycles in the Kirchhoff graph lie in Null($A$) which in this case is

\[
\text{Null}(A) = \text{Span}\left\{ \begin{bmatrix} 1 \\ 0 \\ -1 \\ 2 \end{bmatrix}, \begin{bmatrix} -1 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 2 \\ -1 \\ 0 \\ 0 \end{bmatrix} \right\}, \tag{16}
\]

Again since there are no overall reactions, the vertex current balance conditions are given by the row space of $A$ (for short, the vertices must lie in the row space of $A$).

\[
\text{Row}(A) = \text{Span}\{[1, 2, 1, 0], [0, 1, 2, 1]\}, \tag{17}
\]

Construction of a Kirchhoff graph can be based on a transformation by elementary row operations of the transpose of the stoichiometric matrix for this network to an incidence matrix for the Kirchhoff graph. An incidence matrix for a graph has a positive integral entry $a_{ij}$ in the $i,j$-th position when an edge representing step $i$ is based at vertex $j$ with multiplicity $a_{ij}$. A negative entry represents an edge ending at (heading into) a given vertex. The transformation begins with the reduction of the stoichiometric transpose to a matrix form of the row space bases which satisfies our minimal norm criteria from Section 2.4. Such a basis for Example 2 is given in (17). All zero rows may be discarded. One must then add new rows which are linear combinations of existing rows and which have entries which pair with existing entries to form incidence pairs representing the beginning and ending vertices of an edge (or multiple of an edge) in the Kirchhoff graph. These incidence pairs must also be consistent with the null space requirements for the cycles in the Kirchhoff graph. Again this process is probably best seen in terms of an example:

**Example 2b**: Let us begin with the first basis vector in (17) for the row space and construct the first cycle in (16). The first entry in the first row space basis vector is 1, so there must be a corresponding $-1$ in the (2,1) entry of the incidence matrix. Also since $s_2$ is not in the first cycle, one can try to construct the second vertex without this step. This implies a 0 in the (2,2) position. To achieve both of these results, the second row must be formed by adding twice the second row space basis vector to the negative of the first basis vector. The resulting second row has a 2 in the (2,4) position. Since our cycle has two $s_4$ steps, it is reasonable to place these steps in series with a null-vertex between them. It is often useful to place such a null-vertex at the center of the graph. For the fourth and final vertex in this cycle, it is again reasonable to try to avoid $s_2$; this means that for the fourth row in the incidence matrix, the (4,4) entry must be $-2$ and the (4,2) entry should be 0. This row can only be achieved by subtracting twice the second basis vector in (17) from the first basis vector. The resulting row has a $-3$ in the (4,3) position, and the null-space requirements now force the (1,3) entry to be its incidence pair and thus be 3. This of course does not match the initial first row where the (1,3) entry is 1. If one adds the second basis vector in (17) to the initial first row, however, one obtains a revised first row that does satisfy the requirements for the first cycle in (16). This revision leads to a 3 in the (1,2) position which is unavoidable given the
other requirements so far. The partial incidence matrix constructed so far is

\[
\begin{bmatrix}
1 & 3 & 3 & 1 \\
-1 & 0 & 3 & 2 \\
0 & 0 & 0 & 2 - 2 \\
1 & 0 & -3 & -2 \\
\end{bmatrix}
\]  \quad (18)

The entries which have been paired so far are in bold.

Now the first cycle from the null space basis (16) must be added to the graph and in particular to the partial incidence matrix (18). Starting with the currently unpaired 3 in the (1,2) position in (18), one must construct a fifth row with a \(-3\) in the (5,2) position. In addition, since the first cycle does not contain \(s_3\), one can try to avoid this step in the new row and corresponding vertex by placing a 0 in the (5,3) position. Both of these requirements can be achieved by adding the second basis vector from (17) to the negative of the first basis vector. The resulting row has a \(-2\) in the (5,1) position. Since the first vector in the null space basis (16) contains 2 copies of the first reaction step, it again makes sense to try these in series with a null vertex between them. This may be (but does not necessarily have to be) the same null vertex as the one in the previous cycle. For the moment, let us try to achieve a Kirchhoff graph with only one null vertex. To complete this cycle, one needs a sixth row (and sixth vertex) with a 2 in the (6,1) position and a -1 in the (6,4) position. These results can be achieved if the sixth row is the negative of the fifth. With all of these additional rows, the partial incidence matrix becomes

\[
\begin{bmatrix}
1 & 3 & 3 & 1 \\
-1 & 0 & 3 & 2 \\
2 - 2 & 0 & 0 & 2 - 2 \\
1 & 0 & -3 & -2 \\
-2 & -3 & 0 & 1 \\
2 & 3 & 0 & -1 \\
\end{bmatrix}
\]  \quad (19)

The entries that are paired to form the second cycle are in italics.

Of course the matrix in (19) is not yet an incidence matrix; there are still unpaired entries. But reviewing the these unpaired entries, one finds that they can be paired through a single additional row and the addition of this row is consistent with the null space cycle requirements. One can also note that the rows of the incidence matrix can be permuted so that the resulting matrix is antisymmetric about the null row:

\[
\begin{bmatrix}
1 & 3 & 3 & 1 \\
-1 & 0 & 3 & 2 \\
2 - 2 & 0 & 0 & 2 - 2 \\
1 & 0 & -3 & -2 \\
-2 & -3 & 0 & 1 \\
2 & 3 & 0 & -1 \\
\end{bmatrix}
\]  \quad (20)

The entries in the row that corresponds to the null vertex have been changed in (20) to zeros. Using this incidence matrix, one can construct a Kirchhoff graph, one
version of which is shown in Figure 6. This Kirchhoff graph is inherently nonlinear. It has 7 vertices and 22 edges. Nonetheless it appears to be (up to projection orientations) the simplest Kirchhoff graph for this reaction network.

Of course in the construction above, there were a number of free choices where one could have taken another route and thereby constructed a different matrix or reached an impass indicating that the chosen route did not lead to a valid incidence matrix. If one had reached an impass, it would have been necessary to go back and change one or more of the free choices until a valid incidence matrix is reached. While there is no guarantee that this will always work, experience indicates that at least it often does. This process can be programmed so that a computer could accomplish the search.

In summary, Example 2 suggests a general method for constructing Kirchhoff graphs. Let $A$ now denote the augmented transpose of the stoichiometric matrix (which was denoted as $\tilde{A}$ in Example 1 above). The steps for constructing an incidence matrix and thereby a Kirchhoff graph as follows:

Step 1: Construct all the elements of a cycle basis (a basis for $\text{Null}(A)$) which satisfies the minimal total norm requirement.

Step 2: Construct a minimal total norm basis for the row space of $A$.

Step 3: Starting from the matrix whose rows are the basis in Step 2 use row operations to construct incidence pairs, adding new rows whenever necessary. The incidence pairs must combine to yield elements of the cycle space from Step 1. As in both Example 1 and Example 2, it may be necessary to introduce one or more null vertices (a rows of zeros) to form an incidence matrix which is consistent with the cycle basis.
Step 4: If all vertices now satisfy Kirchhoff laws, the construction is complete. If not, return to Step 3 and re-pair the elements of the cycle basis (changing which elements are adjacent to each other). If an incidence matrix still can not be achieved, return to Steps 1 and 2 and consider another basis which satisfies (or nearly satisfies) the minimal norm requirement.

5 Conclusion

Perhaps the most interesting outcome of this work is the conjecture that at least one Kirchhoff graph exists for every matrix, not just those associated with reaction networks. While there is no attempt here to fully study matrices and their Kirchhoff graphs, a number of concluding observations seem to be in order. There are two extreme cases (which do not correspond to reaction networks) to consider first, followed by a number of other interesting cases:

- For the zero matrix (any dimension), the Kirchhoff graph is a single vertex with no edges. Similarly if \( A \) is a matrix with only one linearly independent row, then the null space conditions imply that all the edges are scalar multiples of a single edge. Since every Kirchhoff graph is a cycle, the only possibility is again the degenerate case with one vertex and no edges.

- At the other extreme, suppose \( \text{Null}(A) = \emptyset \). Then the only possible cycle is a null cycle, and such a cycle can always be constructed. To see this, let \( A \) be an \( n \times m \) matrix; then \( \text{Null}(A) = \emptyset \) implies \( n \geq m \) and there must be \( m \) linearly independent rows. Row operations can reduce this to an \( m \times m \) diagonal block, and from this block, row operations can generate the incidence matrix for a single null cycle where all of the steps cancel. As always, there is no claim that this Kirchhoff graph is unique.

Example 3:

\[
A = \begin{bmatrix}
1 & 0 & 0 \\
0 & 2 & 0 \\
0 & 0 & -1 \\
0 & 0 & 0
\end{bmatrix}
\rightarrow \begin{bmatrix}
1 & 0 & -1 \\
-1 & 2 & 0 \\
0 & -2 & -1 \\
-1 & 0 & 1
\end{bmatrix}.
\] (21)

The incidence pairs are each diagonal entry in each \( 3 \times 3 \) block and the opposite signed entry just below. The corresponding null cycle is presented in Figure 7.

- The examples so far might make one think that Kirchhoff graphs are always symmetric; this is not the case.

Example 4: Suppose

\[
A = \begin{bmatrix}
1 & 0 & 1 \\
-1 & 1 & 0 \\
0 & -1 & -1
\end{bmatrix}.
\] (22)
Then the simplest Kirchhoff graph corresponding to this matrix is

Figure 8: A nonsymmetric Kirchhoff graph for (22).

- It is worth noting that a relatively simple matrix may not have in any sense a simple Kirchhoff graph.

**Example 5:** For the

\[
A = \begin{bmatrix}
1 & 0 & 1 & 1 & 0 & -2 \\
0 & 4 & -1 & 0 & 1 & 0 \\
2 & -1 & 0 & -1 & 0 & 1 \\
0 & 1 & 1 & 2 & 1 & 1
\end{bmatrix}.
\]  

Then

\[
\text{Null}(A) = \text{Span}\{[-3, 2, 11, -8, 3, 0], [1, 1, -1, 2, 3, 1]\}
\]

and the row-reduced form is

\[
\begin{bmatrix}
1 & 0 & 0 & 0 & 1 & 4 \\
0 & 3 & 0 & 0 & -2 & -13 \\
0 & 0 & 3 & 0 & -11 & -52 \\
0 & 0 & 0 & 3 & 8 & 34
\end{bmatrix}.
\]

Therefore a Kirchhoff graph for this matrix would be composed of two cycles one of which has length 27. The Kirchhoff current balance conditions would also be complicated. So there is no guarantee that a relatively small matrix (or a relatively small reaction network) will have a simple Kirchhoff graph.
Returning to the connections between reaction networks and Kirchhoff graphs, it is worth presenting a somewhat complicated reaction network which is more easily understood in terms of a Kirchhoff graph. In some sense this is the inverse of Example 5 where the Kirchhoff graph is if anything more complicated than the matrix it is based on. Consider the following reaction network for methanol decomposition on Pt(111) in a direct methanol fuel cell [22]:

\[
\begin{align*}
   s_1 : & \quad \text{CH}_3\text{OH} + S \rightleftharpoons \text{CH}_3\text{OH} \cdot S, \\
   s_2 : & \quad \text{CH}_3\text{OH} \cdot S + S \rightleftharpoons \text{CH}_3\text{O} \cdot S + \text{H} \cdot S, \\
   s_3 : & \quad \text{CH}_3\text{O} \cdot S + 2S \rightleftharpoons \text{CH}_3\text{O} \cdot S_2 + \text{H} \cdot S, \\
   s_4 : & \quad \text{CH}_3\text{O} \cdot S_2 \rightleftharpoons \text{CHO} \cdot S + \text{H} \cdot S, \\
   s_5 : & \quad \text{CHO} \cdot S \rightleftharpoons \text{CO} \cdot S + \text{H} \cdot S, \\
   s_6 : & \quad \text{CH}_3\text{OH} \cdot S + S \rightleftharpoons \text{CH}_2\text{OH} \cdot S + \text{H} \cdot S, \\
   s_7 : & \quad \text{CH}_2\text{OH} \cdot S + S \rightleftharpoons \text{CHOH} \cdot S + \text{H} \cdot S, \\
   s_8 : & \quad \text{CHOH} \cdot S + S \rightleftharpoons \text{COH} \cdot S + \text{H} \cdot S, \\
   s_9 : & \quad \text{COH} \cdot S + S \rightleftharpoons \text{CO} \cdot S + \text{H} \cdot S, \\
   s_{10} : & \quad \text{CHOH} \cdot S + 2S \rightleftharpoons \text{CO} \cdot S + 2\text{H} \cdot S, \\
   s_{11} : & \quad \text{CH}_2\text{OH} \cdot S + 2S \rightleftharpoons \text{CH}_2\text{O} \cdot S_2 + \text{H} \cdot S, \\
   s_{12} : & \quad \text{CO} \cdot S \rightleftharpoons \text{CO} + S, \\
   s_{13} : & \quad \text{H} \cdot S + \text{H} \cdot S \rightleftharpoons \text{H}_2 + 2S,
\end{align*}
\]

(26)

Vilekar, Fishtik & Datta (2007) have presented a Kirchhoff graph for this reaction network and then use the graph to calculate an overall reaction rate and to find a simpler equivalent Kirchhoff graph and corresponding reaction network. Despite the apparent complexity of (26), one finds that there is a single overall reaction, and after this overall reaction is augmented to the network, the null space consists of
four cycles which can be joined together to produce the Kirchhoff graph in Figure 9.

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References


