

# Chemical Reactor Analysis and Design Fundamentals

2nd Edition

**James B. Rawlings**  
Department of Chemical and Biological  
Engineering  
University of Wisconsin  
Madison, Wisconsin

**John G. Ekerdt**  
Department of Chemical Engineering  
The University of Texas  
Austin, Texas

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## 2

### The Stoichiometry of Reactions

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#### 2.1 Introduction

Stoichiometry is defined as the determination of the proportions in which chemical elements combine or are produced and the weight relations in any chemical reaction.<sup>1</sup> In this chapter we explore and develop these quantitative relations between the different chemical species undergoing chemical reaction.

The next section establishes the accounting procedure for tracking chemical change and introduces the stoichiometric matrix. Section 2.3 introduces the concept of linearly independent reactions and discusses the implications of mass conservation on the stoichiometric matrix. Section 2.4 defines the rates of reactions and rates of production of chemical species due to the reactions. Section 2.5 explores the issues involved in calculating production rates given reaction rates and vice versa. We also formulate and solve the least-squares problem of extracting best estimates of reaction rates given production rate measurements containing errors.

Section 2.6 provides a summary of the important concepts and relationships that may prove useful as a study guide or quick reference. References for further study are provided at the end of the chapter. Exercises are provided in Section 2.7 for reinforcing the concepts and to further develop one's understanding. The last several exercises introduce new material and show how the stoichiometry fundamentals presented in this chapter lead into other interesting topics. The reactor analysis book by Aris [1] influenced several sections of this chapter.

<sup>1</sup>Webster's New World College Dictionary, fifth edition, 2004.

## 2.2 Chemical Reactions and Stoichiometry

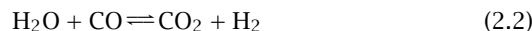
We shall consider three primary examples as a means of illustrating the main concepts in this chapter. The first example is one of the reactions responsible for smog formation in the atmosphere. It consists of a single reaction among three species. The second example is the water gas shift reaction, and it illustrates the case of multiple reactions; it consists of three reactions among six chemical species. The third example illustrates the complexity of common industrial reactions of interest, consisting of 20 reactions among 14 species. These reactions have been proposed to describe a silicon chemical vapor deposition process, which is an important step in the production of microelectronic materials.

For the first example, consider two molecules of nitric oxide and one molecule of oxygen reacting to form two molecules of nitrogen dioxide. The stoichiometry of this reaction is



The convention that we follow is reactants appear on the left-hand side of the chemical reaction symbol,  $\rightleftharpoons$ , and products appear on the right-hand side. In this example, there is a single chemical reaction and three different chemical species taking part in the reaction, NO, O<sub>2</sub>, and NO<sub>2</sub>.

The second example is known as the water gas shift reaction. The overall stoichiometry of this reaction is

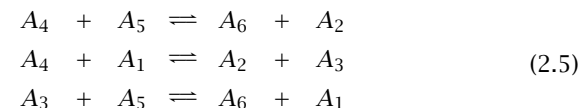


The rate of this reaction is important in determining the CO/CO<sub>2</sub> ratio in exhaust gases from internal combustion engines, and in determining the H<sub>2</sub> content in the feed for fuel cells. It also is known that the following two reactions are needed to describe what is happening at the molecular level,



Reactions 2.2–2.4 comprise a simple reaction network. There are three chemical reactions and six different chemical species taking part in the three reactions, H, H<sub>2</sub>, OH, H<sub>2</sub>O, CO, and CO<sub>2</sub>.

In order to organize the way we discuss chemical reactions, the following notation is convenient. Let the symbol,  $A_j$ , represent the  $j$ th species taking part in a reaction. In the first example, we can choose  $A_1 = \text{NO}$ ,  $A_2 = \text{O}_2$ , and  $A_3 = \text{NO}_2$ . In the water gas shift example, we can choose  $A_1 = \text{H}$ ,  $A_2 = \text{H}_2$ ,  $A_3 = \text{OH}$ ,  $A_4 = \text{H}_2\text{O}$ ,  $A_5 = \text{CO}$ , and  $A_6 = \text{CO}_2$ . Using the  $A_j$  notation, we can express the water gas shift reactions as



Reactions 2.5 suppress the identities of the species for compactness. We can further compress the description by moving all of the *variables* to the right-hand side of the chemical reaction symbol and replacing it with an equality sign,

$$\begin{aligned} -A_4 - A_5 + A_6 + A_2 &= 0 \\ -A_4 - A_1 + A_2 + A_3 &= 0 \\ -A_3 - A_5 + A_6 + A_1 &= 0 \end{aligned} \quad (2.6)$$

Again notice the sign convention that **products** have **positive** coefficients and **reactants** have **negative** coefficients in Equations 2.6.<sup>2</sup> Equations 2.6 now resemble a set of three linear algebraic equations and motivates the use of matrices. Using the rules of matrix multiplication, one can express Equations 2.6 as

$$\begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad (2.7)$$

The matrix appearing in Equation 2.7 provides an efficient description of the stoichiometry for the reaction network, and is appropriately known as the **stoichiometric matrix**. Giving the stoichiometric matrix the symbol  $\mathbf{v}$ , and writing  $\mathbf{A}$  to denote the column vector of the  $A_j$ ,  $j = 1, \dots, 6$ , our final summary of the water gas shift reaction appears as

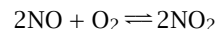
$$\mathbf{v}\mathbf{A} = \mathbf{0}$$

<sup>2</sup>Boldface letters provide a mnemonic device.

The element  $v_{ij}$  in the stoichiometric matrix is the stoichiometric coefficient for the  $j$ th species in the  $i$ th reaction. The index  $i$  runs from 1 to  $n_r$ , the total number of reactions in the network, and the index  $j$  runs from 1 to  $n_s$ , the total number of species in the network. We say that  $\mathbf{v}$  is an  $n_r \times n_s$  matrix. After piling up this much abstraction to describe what started out as a simple set of three reactions, let us work a few examples to reinforce the concept of the stoichiometric matrix.

### Example 2.1: Stoichiometric matrix for a single reaction

Find the stoichiometric matrix for the nitric oxide example,



#### Solution

The nitric oxide example consists of one reaction and three species. We can assign the species to the  $A$  as follows:  $A_1 = \text{NO}$ ,  $A_2 = \text{O}_2$ ,  $A_3 = \text{NO}_2$ . The reaction can then be written as

$$-2A_1 - A_2 + 2A_3 = \begin{bmatrix} -2 & -1 & 2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = 0$$

The stoichiometric matrix for a single reaction is a row vector, in this case,

$$\mathbf{v} = \begin{bmatrix} -2 & -1 & 2 \end{bmatrix}$$

□

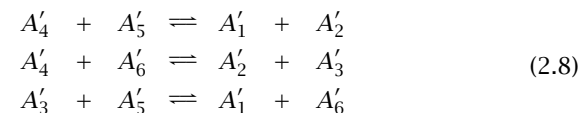
### Example 2.2: Columns of $\mathbf{v}$

Since we are free to assign chemical species to the  $A_j$  in any order we choose, consider what happens if we change the order of the species in the water gas shift example. Instead of using  $A_1 = \text{H}$  and  $A_6 = \text{CO}_2$ , what is the stoichiometric matrix if  $A_1$  is chosen to be  $\text{CO}_2$  and  $A_6$  is chosen to be  $\text{H}$ ?

#### Solution

Switching the identities of the first and sixth species in the  $A$  vector gives us the following modified vector,  $A'_1 = \text{CO}_2$ ,  $A'_2 = \text{H}_2$ ,  $A'_3 = \text{OH}$ ,

$A'_4 = \text{H}_2\text{O}$ ,  $A'_5 = \text{CO}$ , and  $A'_6 = \text{H}$ . Reactions 2.5 are then modified to give



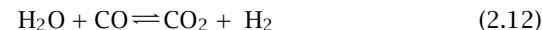
Extracting the modified  $\mathbf{v}$  matrix from Equations 2.8 gives

$$\mathbf{v}' = \begin{array}{cccccc} & \downarrow & & & & \downarrow \\ \begin{bmatrix} 1 & 1 & 0 & -1 & -1 & 0 \\ 0 & 1 & 1 & -1 & 0 & -1 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} & & & & & \end{array} \quad (2.9)$$

It is clear from examining Equations 2.9 and 2.7 that switching the identities of species one and six in the  $A$  vector has necessitated switching the first and sixth *columns* in the stoichiometric matrix. Therefore one can make the connection between the *columns* of  $\mathbf{v}$  and the *species* taking part in the reactions. More precisely, the  $j$ th column of the  $\mathbf{v}$  matrix supplies the stoichiometric numbers of the  $j$ th species in all of the reactions. □

### Example 2.3: Rows of $\mathbf{v}$

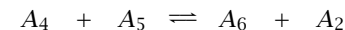
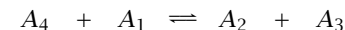
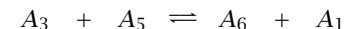
Just as we are free to assign the species to the  $A$  vector in any order we choose, we are also free to express the reactions in any order we choose. We now explore what happens if instead of expressing the water gas shift reaction as it appears in Reactions 2.2–2.4, we express it as



Notice we have written the original third reaction first and the original first reaction third. What is the impact of this change on the  $\mathbf{v}$  matrix?

#### Solution

Using the original ordering of the  $A$  vector, we can ascribe the following elements of a third stoichiometric matrix,

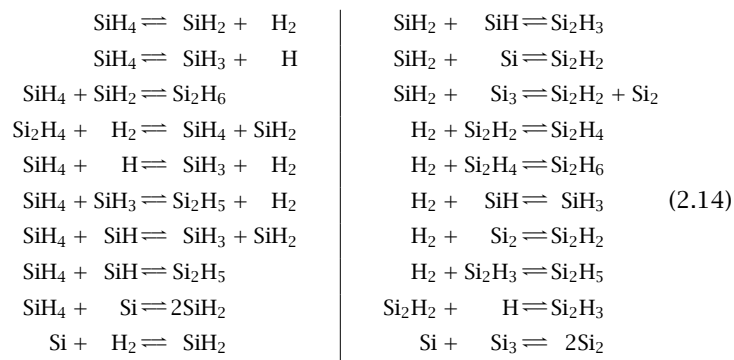


$$\mathbf{v}'' = \begin{matrix} \rightarrow \\ \rightarrow \\ \rightarrow \end{matrix} \begin{bmatrix} 1 & 0 & -1 & 0 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & -1 & 1 \end{bmatrix} \quad (2.13)$$

As one might expect, exchanging the orders of the first and third reactions causes us to exchange the first and third rows in the  $\mathbf{v}$  matrix as evidenced by comparing the matrices in Equations 2.13 and 2.7. We can therefore make the connection between the rows of  $\mathbf{v}$  and the reactions.<sup>3</sup> The  $i$ th row of the stoichiometric matrix contains the stoichiometric numbers of all species in the  $i$ th reaction.  $\square$

From the previous two examples it is clear that one could develop a large number of stoichiometric matrices to describe the same set of chemical reactions. Since there is no reason to prefer one ordering of species and reactions over another, one may permute the columns and rows into any order and maintain a valid stoichiometric matrix.

We now introduce the third example, which is a more complicated reaction network. The following chemistry has been proposed to describe a silicon chemical vapor deposition (CVD) reaction, which is an important process in the production of microelectronic materials.



The student should not be dismayed by the complexity of this reaction network. Indeed the principles for analyzing a CVD reactor with this chemistry are exactly the same as the principles for analyzing the

<sup>3</sup>Another mnemonic.

simpler nitric oxide and water gas shift chemistries presented previously. The only difference is that Reactions 2.14 are complex enough that we use a computer to keep track of the algebra for us. In fact, Reactions 2.14 are a simplified version of 120 reactions that were originally postulated for this reaction network [3].

Chemical engineers should also bear in mind that Reactions 2.14 are quite simple compared to many mechanisms that have been proposed for combustion problems in which it is not uncommon to have several hundred reactions. Polymerizations and long-chain-producing reactions consist of thousands of species and associated reactions. Obviously the stoichiometry of these complex problems is intractable if we do not develop a systematic, automated procedure. Developing and understanding that procedure is the topic of the next several sections.

#### Example 2.4: Stoichiometric matrix for CVD chemistry

Determine the stoichiometric matrix corresponding to Reactions 2.14.

#### Solution

The first thing we notice is that there are 20 reactions or  $n_r = 20$ . We then look through all of the reactions and identify the different species taking part. After writing this out we notice that there are 14 different species,  $n_s = 14$ . A possible assignment to the  $\mathbf{A}$  vector is: H, H<sub>2</sub>, Si, SiH, SiH<sub>2</sub>, SiH<sub>3</sub>, SiH<sub>4</sub>, Si<sub>2</sub>, Si<sub>2</sub>H<sub>2</sub>, Si<sub>2</sub>H<sub>3</sub>, Si<sub>2</sub>H<sub>4</sub>, Si<sub>2</sub>H<sub>5</sub>, Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>. With an  $\mathbf{A}$  chosen, it is a simple matter to look through Reactions 2.14 and find the stoichiometric coefficients of each species in each reaction. Do not forget the convention that species appearing as products in a given reaction have positive coefficients and those appearing as reactants have negative coefficients. Practice filling out a few rows of the  $\mathbf{v}$  matrix and check it with the values given in Equation 2.15.

Notice that for this example  $\mathbf{v}$  is a  $20 \times 14$  matrix, and it contains many zero entries. A matrix with many zero entries is called sparse. The large number of zeros simply reflects the physical fact that very few molecules can take part in a particular reaction. All of the reactions in the CVD chemistry, for example, are unimolecular or bimolecular. More will be said about this issue in the discussion of mechanisms in Chapter 5.

$$\mathbf{v} = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \quad (2.15)$$

□

**Example 2.5: Conservation of mass**

Show that conservation of mass in a chemical reaction can be stated as

$$\mathbf{vM} = \mathbf{0}$$

in which  $M_j$  is the molecular weight of species  $j$ .

**Solution**

In a chemical reaction, the number of molecules is not conserved in general. For example in the nitric oxide reaction,  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ , *three* reactant molecules react to form *two* product molecules. The mass, however, is conserved in chemical (i.e., not nuclear) reactions. It is clear in the above example that the atoms (N and O) are conserved, so the mass is conserved. Another way to state conservation of mass involves molecular weights of the species. In the nitric oxide reaction, the molecular weights of reactants and products are related by  $2M_{\text{NO}} +$

$M_{\text{O}_2} = 2M_{\text{NO}_2}$ . Equivalently

$$-2M_{\text{NO}} - M_{\text{O}_2} + 2M_{\text{NO}_2} = \begin{bmatrix} -2 & -1 & 2 \end{bmatrix} \begin{bmatrix} M_{\text{NO}} \\ M_{\text{O}_2} \\ M_{\text{NO}_2} \end{bmatrix} = 0$$

If we put the molecular weights of the species in a vector,  $\mathbf{M}$ , conservation of mass for this single reaction can be written as,

$$\mathbf{vM} = 0$$

For the water gas shift reaction, using the ordering of the species,  $A_1 = \text{H}$ ,  $A_2 = \text{H}_2$ ,  $A_3 = \text{OH}$ ,  $A_4 = \text{H}_2\text{O}$ ,  $A_5 = \text{CO}$ , and  $A_6 = \text{CO}_2$ ,

$$\mathbf{M} = \begin{bmatrix} M_{\text{H}} & M_{\text{H}_2} & M_{\text{OH}} & M_{\text{H}_2\text{O}} & M_{\text{CO}} & M_{\text{CO}_2} \end{bmatrix}^T$$

in which the superscript  $T$  means the transpose of the matrix. The transpose of the matrix means to exchange the rows for columns and vice versa. For the first reaction,  $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$ , we know

$$M_{\text{CO}_2} + M_{\text{H}_2} - M_{\text{H}_2\text{O}} - M_{\text{CO}} = 0$$

or

$$\begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \end{bmatrix} \begin{bmatrix} M_{\text{H}} \\ M_{\text{H}_2} \\ M_{\text{OH}} \\ M_{\text{H}_2\text{O}} \\ M_{\text{CO}} \\ M_{\text{CO}_2} \end{bmatrix} = 0$$

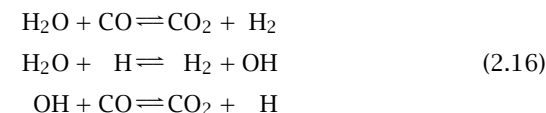
which is the first row of  $\mathbf{v}$  in Equation 2.7 multiplied by  $\mathbf{M}$ . The second and third reactions simply fill out the second and third rows of  $\mathbf{v}$  so that again, for multiple reactions

$$\mathbf{vM} = \mathbf{0}$$

□

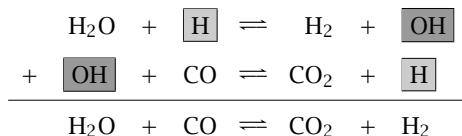
**2.3 Independent Reactions**

To motivate the discussion of independence of chemical reactions, let us again consider the water gas shift reaction

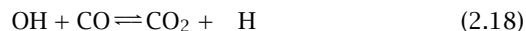




The issue of independence centers on the question of whether or not we can express any reaction in the network as a linear combination of the other reactions. If we can, then the set of reactions is not independent. It is not necessary to eliminate extra reactions and work with the smallest set, but it is sometimes preferable. In any case, the concept is important and is examined further. Before making any of these statements precise, we explore the question of whether or not the three reactions listed in Reactions 2.16 are independent. Can we express the first reaction as a linear combination of the second and third reactions? By *linear* combination we mean multiplying a reaction by a number and adding it to the other reactions. It is clear from inspection that the first reaction is the sum of the second and third reactions, so the set of three reactions is not independent.

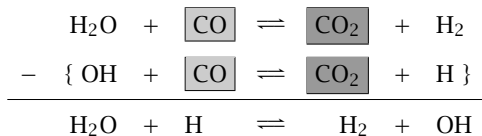


If we deleted the first reaction from the network, would the remaining two reactions be independent?



The answer is now yes, because no multiple of Reaction 2.17 can equal Reaction 2.18. There is no way to produce CO or CO<sub>2</sub> from only Reaction 2.17. Likewise there is no way to produce H<sub>2</sub> or H<sub>2</sub>O from only Reaction 2.18.

This discussion is *not* meant to imply that there is something *wrong* with the first reaction in Reactions 2.16. Indeed if we focus attention on the second reaction, we can again ask the question whether or not it can be written as a linear combination of the first and third reactions. The answer is yes because the second reaction is the first reaction minus the third reaction.



So the first and third reactions could be chosen as the independent set of two reactions. Finally, the third reaction in Reaction 2.16 is equal to the first reaction minus the second reaction, so the first and second reactions could be chosen as an independent set. For this example then, any two of the reactions comprise an independent set. The situation is not always this simple as we will see from the chemical vapor deposition chemistry.

Before making the problem more complicated, we explore how to automate the preceding analysis by exploiting the stoichiometric matrix. If you are familiar with linear algebra, the issue of independence of reactions is obviously related to the rank of the stoichiometric matrix. Familiarity with these concepts, although helpful, is not required to follow the subsequent development. We now consider the stoichiometric matrix for the water gas shift reaction presented in Equation 2.7

$$\mathbf{v} = \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \quad (2.19)$$

We can make an important mathematical connection to the preceding physical arguments. The question of whether or not the *i*th reaction can be written as a linear combination of the other reactions is the same as the question of whether or not the *i*th row of the  $\mathbf{v}$  matrix can be written as a linear combination of the other rows. The linear independence of the reactions in a reaction network is equivalent to the linear independence of the rows in the corresponding stoichiometric matrix.

The **rank** of a matrix is defined as the number of linearly independent rows (or equivalently, columns) in the matrix. Therefore, the number of linearly independent reactions in a network,  $n_i$ , is equal to the rank of  $\mathbf{v}$ . There are efficient numerical algorithms available for finding the rank of a matrix and a set of linearly independent rows. The focus of our attention is not on the algorithm, but on how we can exploit the results of the algorithm to analyze sets of chemical reactions. You should consult Strang [7] or another linear algebra text for a lucid explanation of the algorithm, Gaussian elimination with partial pivoting.

#### Example 2.6: More species than reactions

Show that mass conservation implies that any *independent* set of reactions has more species than reactions.

**Solution**

From Example 2.5, we know that mass conservation is equivalent to

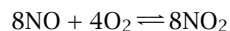
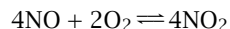
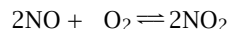
$$\mathbf{vM} = \mathbf{0}$$

Consider the columns of the  $\mathbf{v}$  matrix as column vectors. This matrix-vector multiplication can be expressed as a linear combination of the columns of  $\mathbf{v}$  with the elements of the  $\mathbf{M}$  vector as the coefficients in the linear combination

$$\begin{aligned} \mathbf{vM} &= \begin{bmatrix} v_{11} & v_{12} & \cdots & v_{1n_s} \\ \vdots & \vdots & \ddots & \vdots \\ v_{n_i1} & v_{n_i2} & \cdots & v_{n_in_s} \end{bmatrix} \begin{bmatrix} M_1 \\ M_2 \\ \vdots \\ M_{n_s} \end{bmatrix} \\ &= \begin{bmatrix} v_{11} \\ \vdots \\ v_{n_i1} \end{bmatrix} M_1 + \begin{bmatrix} v_{12} \\ \vdots \\ v_{n_i2} \end{bmatrix} M_2 + \cdots + \begin{bmatrix} v_{1n_s} \\ \vdots \\ v_{n_in_s} \end{bmatrix} M_{n_s} \\ &= \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix} \end{aligned} \quad (2.20)$$

The last equation implies the columns of  $\mathbf{v}$  are linearly *dependent* because the molecular weights are nonzero.<sup>4</sup> Because the rows are linearly independent, we conclude there are more columns (species) than rows (independent reactions),  $n_s > n_i$  and  $\mathbf{v}$  is a *wide* matrix (i.e., not a square or *tall* matrix).

Notice that one must consider linearly independent reactions for the statement in the example to be true. If we considered an arbitrary network for example,



<sup>4</sup>One could solve for column  $j$  of  $\mathbf{v}$  by moving the remaining terms to the other side of the equality and dividing by  $M_j$ , which is nonzero. That is possible as long as one of the  $M_j$  multipliers in Equation 2.20 is nonzero. In our case, all of the multipliers are nonzero.

These reactions are obviously not independent because they are the same reaction written four times. In this case

$$\mathbf{v} = \begin{bmatrix} -2 & -1 & 2 \\ -4 & -2 & 4 \\ -6 & -3 & 6 \\ -8 & -4 & 8 \end{bmatrix}$$

Since we have not used independent reactions,  $\mathbf{v}$  is *tall* and not *wide*. Recall  $\mathbf{v} = \begin{bmatrix} -2 & -1 & 2 \end{bmatrix}$  for the single independent reaction, which is in agreement with the example.  $\square$

**Maximal sets of linearly independent reactions.** Up to this point, we have started with a set of reactions and investigated constructing subsets of these reactions that are linearly independent. Now consider the reverse problem. We start with a set of species, and we would like to know the largest number of linearly independent valid chemical reactions among these species. In other words, a given set of reactions may be linearly independent, but we want to be sure we have not left out some valid reactions. By valid chemical reactions we mean *element conserving*, which is a sufficient condition implying the weaker condition of *mass conserving*.

The following describes a systematic approach to this problem. First, list formation reactions for every species in the list from its elements. We may use molecules of pure elements ( $\text{O}_2$ ) rather than atoms ( $\text{O}$ ) to save work as long as the atoms themselves do not appear in the species list. This set is guaranteed by construction to be a maximal linearly independent set for an *enlarged* species list, which includes the original species plus any new elements introduced in the formation reactions.

Then eliminate through linear combinations of reactions any new elements that were introduced in the formation reactions and that do not appear in the original species list. The remaining set is a maximal linearly independent set of reactions for the original species list.

This procedure is perhaps best illustrated by example.

**Example 2.7: Maximal set of reactions for methane oxidation**

Consider the oxidation of methane in which the observed species are:

$$\mathbf{A} = \begin{bmatrix} \text{CO}_2 & \text{H}_2\text{O} & \text{CH}_4 & \text{CO} & \text{H}_2 & \text{O}_2 \end{bmatrix}^T$$

We first write formation reactions for all species from the elements. It is necessary to write these reactions in the order in which the species

appear in the species list. We can use  $O_2$  and  $H_2$  because O and H are not in the species list



Notice we have introduced the element carbon, which is not in the original species list, to express the formation reactions. We can add C to the list and the enlarged species list is

$$\tilde{A} = [CO_2 \quad H_2O \quad CH_4 \quad CO \quad H_2 \quad O_2 \quad C]^T$$

The stoichiometry of the formation reactions are then summarized by

$$\tilde{\mathbf{v}}\tilde{A} = \mathbf{0}$$

in which

$$\tilde{\mathbf{v}} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & -1 & -1 \\ 0 & 2 & 0 & 0 & -2 & -1 & 0 \\ 0 & 0 & 1 & 0 & -2 & 0 & -1 \\ 0 & 0 & 0 & 2 & 0 & -1 & -2 \end{bmatrix} \quad (2.25)$$

Notice we have zeros below the diagonal of the first four rows and columns. We know *by inspection* that these reactions are linearly independent, which is why we wrote them in the first place.<sup>5</sup> So the rank of  $\tilde{\mathbf{v}}$  is four. See Exercise 2.9 for a proof that there are no other valid linearly independent reactions among these species and elements.

We now wish to eliminate carbon from the species list. The approach is to replace formation reactions involving C with independent linear combinations of the four reactions that eliminate C from the set. For example we could replace Reaction 2.21 with the sum of Reaction 2.21 and the negative of Reaction 2.23. Equivalently we replace row 1 in Equation 2.25 with the sum of row 1 and negative of row 3. We always add linear combinations of rows *below* the row on which we are making the zero in order not to disturb the pattern of zeros below the diagonal in the first columns of the matrix. We leave the second row unchanged

<sup>5</sup>Examine the locations of the zeros in the first four rows and columns of  $\tilde{\mathbf{v}}$ . Because these portions of the first four rows are independent, so are the entire rows, and, therefore, the reactions.

because the  $v_{2,7}$  is zero already; i.e., C does not take place in the second reaction. Proceeding down the rows we replace row 3 by twice row 3 minus row 4. When we reach the last row, either a zero already exists in the last column or we remove this last row because we have no rows below the last with which to zero that element. That reduces  $\tilde{\mathbf{v}}$  to

$$\tilde{\mathbf{v}}' = \begin{bmatrix} 1 & 0 & -1 & 0 & 2 & -1 & 0 \\ 0 & 2 & 0 & 0 & -2 & -1 & 0 \\ 0 & 0 & 2 & -2 & -4 & 1 & 0 \end{bmatrix}$$

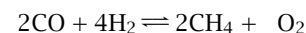
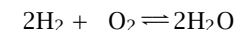
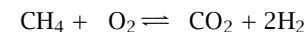
Inspection of the zeros in the first three columns of  $\tilde{\mathbf{v}}'$  tells us that the rows are independent, and, therefore, the matrix has full rank. If we now multiply out these equations, the last column of zeros removes the C from the species list and we have

$$\mathbf{v}A = \mathbf{0}$$

in which

$$\mathbf{v} = \begin{bmatrix} 1 & 0 & -1 & 0 & 2 & -1 \\ 0 & 2 & 0 & 0 & -2 & -1 \\ 0 & 0 & 2 & -2 & -4 & 1 \end{bmatrix}$$

Therefore the maximal linearly independent set for the original species contains *three* reactions. The stoichiometric matrix above corresponds to the following choice of reactions



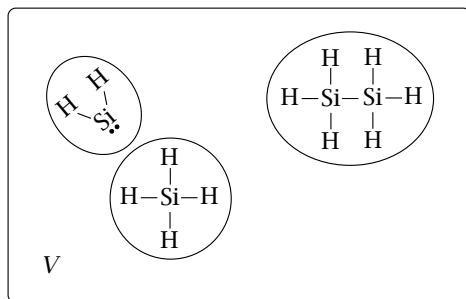
□

If we were going to remove other elements besides C, we would repeat this procedure starting with  $\mathbf{v}$ . See also Exercise 2.6.

## 2.4 Reaction Rates and Production Rates

In order to describe the change in composition in a reactor, one has to know the reaction rates. As an example, we consider the third reaction in the CVD chemistry, Reactions 2.14





**Figure 2.1:** Defining the reaction rate,  $r$ , for the reaction  $\text{SiH}_2 + \text{SiH}_4 \rightleftharpoons \text{Si}_2\text{H}_6$ .

The **reaction rate**,  $r$ , is defined as the number of times this reaction event takes place per time per volume. One can imagine turning  $\text{SiH}_4$ ,  $\text{SiH}_2$  and  $\text{Si}_2\text{H}_6$  molecules loose in a box of some fixed volume  $V$  as depicted in Figure 2.1. We define the **reaction extent**,  $\epsilon$ , to keep track of the number of times this reaction event occurs. Imagine that we could somehow count up the net number of times an  $\text{SiH}_4$  molecule hit an  $\text{SiH}_2$  molecule and turned into an  $\text{Si}_2\text{H}_6$  molecule during a short period of time. The change in the reaction extent,  $\Delta\epsilon$ , is the net number of reaction events that occur in the time interval  $\Delta t$ . The reaction rate is then

$$r = \frac{\Delta\epsilon}{\Delta t V} \quad (2.27)$$

If the forward event (an  $\text{SiH}_4$  molecule and an  $\text{SiH}_2$  molecule turning into an  $\text{Si}_2\text{H}_6$  molecule) occurs more often than the reverse event (an  $\text{Si}_2\text{H}_6$  molecule decomposing into an  $\text{SiH}_4$  molecule and an  $\text{SiH}_2$  molecule), then the change in  $\epsilon$  is positive and the reaction rate is positive. If the reverse event occurs more often than the forward event, then the change in  $\epsilon$  and reaction rate are negative. If the system is at equilibrium, then the change in  $\epsilon$  is zero and the forward and reverse events occur in equal numbers. The extent  $\epsilon$  is a number of molecular change events and therefore the units of  $r$  in Equation 2.27 are  $\# / (\text{time} \cdot \text{volume})$ . If one divides by Avogadro's number, the units of extent are moles and the units of reaction rate are moles/ $(\text{time} \cdot \text{volume})$ , which are the usual units for extent and reaction rate in this text. Finally, we often deal with physical situations in which we assume the

material behaves as a continuum and we can ignore the discrete nature of the molecules. This means we can take the volume  $V$  large enough to average the random fluctuations of the molecules, but small enough that there is negligible spatial variation in the average concentrations of the components or the reaction rate within  $V$ . Under this continuum assumption, we can speak of the reaction rate as defined at a point in space within some larger reacting system or physical reactor equipment.

Notice in the definition of reaction rate, we are taking the reaction stoichiometry *literally*. We are postulating that these collision and transformation events are taking place at the molecular level. These literal reactions are known as **elementary reactions**. We delay a more complete discussion of elementary reactions and reaction mechanisms until Chapter 5. We will also see that for complex reacting systems, it may be difficult to know whether or not a reaction is an elementary reaction. But that is a separate issue, which we take up later, and that issue does not prevent us from defining the reaction rate.

It is difficult to measure reaction rates directly, because we do not directly sense molecular transformation events. We can measure concentrations, however. It is important to connect the reaction rate to the rate of change of the concentrations of the various species in the reactor, which are the quantities we usually care about in a commercial reactor. We define **production rate**,  $R_j$ , as the rate at which the  $j$ th species is produced (moles/ $(\text{time} \cdot \text{volume})$ ) due to the chemical reactions taking place. It is clear looking at the stoichiometry in Reaction 2.26 that each time the forward reaction event occurs, an  $\text{Si}_2\text{H}_6$  molecule is produced. Each time the reverse reaction occurs, an  $\text{Si}_2\text{H}_6$  molecule is consumed. The production rate of  $\text{Si}_2\text{H}_6$ ,  $R_{\text{Si}_2\text{H}_6}$ , is therefore directly related to the reaction rate,

$$R_{\text{Si}_2\text{H}_6} = r$$

Notice that if  $r$  is positive  $R_{\text{Si}_2\text{H}_6}$  is positive as we expect because  $\text{Si}_2\text{H}_6$  is being produced. Similar arguments lead to relating the other production rates to the reaction rate,

$$R_{\text{SiH}_4} = -r$$

$$R_{\text{SiH}_2} = -r$$

Notice that we have three production rates, one for each species, but only one reaction rate, because there is only a single reaction. If we

now introduce the production rate vector,  $\mathbf{R}$ ,

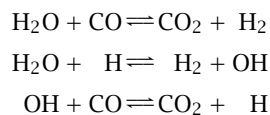
$$\mathbf{R} = \begin{bmatrix} R_{\text{SiH}_4} \\ R_{\text{SiH}_2} \\ R_{\text{Si}_2\text{H}_6} \end{bmatrix}$$

we can summarize the connection between the three production rates and the single reaction rate by

$$\mathbf{R} = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix} r \quad (2.28)$$

Notice that the column vector in Equation 2.28 is just the transpose of the row vector that comprises  $\mathbf{v} = [-1 \ -1 \ 1]$ , which follows from Reaction 2.26

Consider what happens to the relationship between the production and reaction rates if there is more than one reaction. Recall the water gas shift reaction,



Three reaction rates are required to track all three reactions. Let  $r_i$  denote the reaction rate for the  $i$ th reaction. What production rate of atomic hydrogen, H, results from these three reactions? We notice that H does not take part in the first reaction, is consumed in the second reaction, and is produced in the third reaction. We therefore write

$$R_{\text{H}} = (0) r_1 + (-1) r_2 + (1) r_3 = -r_2 + r_3$$

Consider the second species,  $\text{H}_2$ . It is produced in the first and second reactions and does not take part in the third reaction. Its production

rate can therefore be expressed as

$$R_{\text{H}_2} = (1) r_1 + (1) r_2 + (0) r_3 = r_1 + r_2$$

You should examine the remaining four species and produce the following matrix equation,

$$\begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} 0 & -1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \\ -1 & -1 & 0 \\ -1 & 0 & -1 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} \quad (2.29)$$

The fundamental relationship between the reaction rates and the production rates now emerges. Compare the matrices in Equations 2.7 and 2.29. Notice that the first *row* of the matrix in Equation 2.7 is the same as the first *column* of the matrix in Equation 2.29. Moreover, *each* row of the matrix in Equation 2.7 is the same as the corresponding column of the matrix in Equation 2.29. In other words, the two matrices are transposes of each other. We can therefore summarize Equation 2.29 as

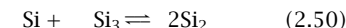
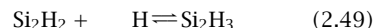
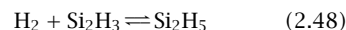
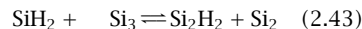
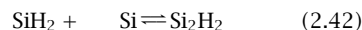
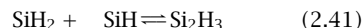
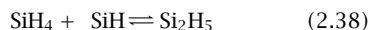
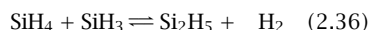
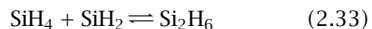
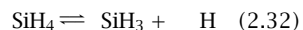
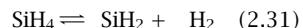
$$\boxed{\mathbf{R} = \mathbf{v}^T \mathbf{r}} \quad (2.30)$$

in which  $\mathbf{v}^T$  denotes the transpose of the stoichiometric matrix. Equation 2.30 implies that one can always compute the production rates from the reaction rates. That computation is a simple matter of matrix multiplication. The reverse problem, deducing the reaction rates from the production rates, is not so simple as it involves solving a set of equations. We will see in the next section under what conditions that solution can be found.

### Example 2.8: Production rate for $\text{SiH}_2$

What is the production rate of  $\text{SiH}_2$  in terms of the reaction rates for the CVD example?

## Solution



Looking at Reactions 2.31–2.50, we note that  $\text{SiH}_2$  takes part in Reactions 2.31, 2.33, 2.34, 2.37, and 2.39–2.43. Extracting the stoichiometric numbers of  $\text{SiH}_2$  for each of these reactions gives<sup>6</sup>

$$R_{\text{SiH}_2} = r_1 - r_3 + r_4 + r_7 + 2r_9 + r_{10} - r_{11} - r_{12} - r_{13}$$

or

$$R_{\text{SiH}_2} = \begin{bmatrix} 1 & 0 & -1 & 1 & 0 & 0 & 1 & 0 & 2 & 1 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \mathbf{r}$$

$\text{SiH}_2$  was chosen as the fifth species in Exercise 2.4 so the row vector above is indeed the transpose of the fifth column of the  $\mathbf{v}$  matrix in Equation 2.15. You may wish to choose another component such as  $\text{SiH}_4$  and check another column of the  $\mathbf{v}$  matrix.  $\square$

## 2.5 Computational Aspects of Stoichiometry

As we have seen in this chapter, problems of realistic and complex reaction stoichiometry involve matrices and linear algebra. After the fundamental concepts are in place, application of the fundamentals requires computational tools. Moreover, if the computing environment is organized properly, the experience of solving nontrivial problems reinforces the understanding of the fundamental concepts and further

<sup>6</sup>We are so sure you will not forget that products have positive stoichiometric numbers and reactants have negative ones that we will not repeat it again.

prepares one to apply the fundamentals in realistic and complex industrial situations. In Appendix A, we briefly summarize Octave and MATLAB as high-level programming languages for numerical solution of reactor analysis and design problems. Octave is freely available for a variety of hardware platforms and can be downloaded from [www.octave.org](http://www.octave.org). MATLAB is commercially available from The MathWorks, Inc., and is becoming a commonly available tool of industrial engineering practice.

### 2.5.1 Computing Production Rates from Reaction Rates

As discussed previously, computing  $\mathbf{R}$  from  $\mathbf{r}$  is a simple matter of matrix multiplication. Consider again the water gas shift reaction chemistry,

$$\begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} \text{H} \\ \text{H}_2 \\ \text{OH} \\ \text{H}_2\text{O} \\ \text{CO} \\ \text{CO}_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad (2.51)$$

In Chapter 5 we discuss means for predicting reaction rates given species concentrations, but for now just assume we know the three reaction rates are, in some chosen units of moles/(time·volume),

$$\begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$$

The production rates of the six species due to these reactions are then computed as

$$\begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix}^T \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 1 \\ 3 \\ -1 \\ -3 \\ -4 \\ 4 \end{bmatrix}$$

The effect of the three reactions is to produce H,  $\text{H}_2$  and  $\text{CO}_2$ , and to consume OH,  $\text{H}_2\text{O}$  and CO at the given rates. Please perform this calculation for yourself.

### 2.5.2 Computing Reaction Rates from Production Rates

Another common task arising in the analysis of reactors and reaction mechanisms is to measure production rates by monitoring changes in species concentrations, to help infer the corresponding reaction rates. To make the concept clear, consider the simple isomerization reactions between species A, B and C,



The stoichiometric matrix for these reactions is

$$\mathbf{v} = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 1 & 0 & -1 \end{bmatrix}$$

and the production rates and reaction rates are related by

$$\begin{bmatrix} R_A \\ R_B \\ R_C \end{bmatrix} = \begin{bmatrix} -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix}$$

It might appear at first glance that we can compute  $\mathbf{r}$  given  $\mathbf{R}$  because we have three equations and three unknowns, but because the reactions are not linearly independent, such is not the case. It is clear from inspection of Reactions 2.52-2.54 that the third reaction is the sum of the first two. Computing the rank of  $\mathbf{v}$  confirms that only two reactions are independent.

Before we continue with the full set of three reactions, we explore what happens if we use an independent set. If we omit the third reaction, for example,



the production rates and new reaction rates are related by

$$\begin{bmatrix} R_A \\ R_B \\ R_C \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \hat{r}_1 \\ \hat{r}_2 \end{bmatrix}$$

By inspection, the first equation gives

$$\hat{r}_1 = -R_A$$

and the third equation gives

$$\hat{r}_2 = R_C$$

The second equation tells us  $R_B = \hat{r}_1 - \hat{r}_2 = -(R_A + R_C)$ . In other words, using the linearly independent reactions, we can compute both reaction rates and we find a restriction on the possible production rates. We explore subsequently what happens when this restriction is violated by the production-rate measurements.

If we now return to the original set of three isomerization reactions, we can deduce that  $r_3$  is not determined by the production rates, and that from the first equation

$$r_1 = -R_A + r_3 \quad (2.55)$$

and from the third equation

$$r_2 = R_C + r_3 \quad (2.56)$$

and  $r_3$  is arbitrary. The second equation places the restriction  $R_B = r_1 - r_2$ , which upon substitution of Equations 2.55 and 2.56 gives  $R_B = -(R_A + R_C)$  as before. Because  $r_3$  is arbitrary, we cannot deduce the reaction rates from production rates, which is characteristic of using sets of reactions that are not linearly independent.

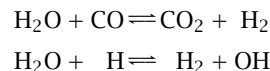
So we conclude that measuring production rates is not enough to tell us reaction rates. We require more information. As we discuss in Chapter 5, the extra information usually is provided by postulating a reaction mechanism and applying the laws of mass action to the elementary reactions. In that case we seek to determine the rate *constants* from the production rate measurements, not the reaction rates themselves. We take up that important problem in Chapter 9.

Finally, we emphasize that using linearly dependent sets of reactions presents no problem at all if one is interested only in computing the production rates from given reaction rates, which is the usual case when working with reaction mechanisms.

### 2.5.3 Measurement Errors and Least-Squares Estimation

As a final topic in this chapter, we explore what happens when the extra conditions on the production rates are violated by the data. Imagine

the following two linearly independent reactions of the water gas shift are taking place



so the production rates are given by

$$\begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 1 & 1 \\ 0 & 1 \\ -1 & -1 \\ -1 & 0 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \end{bmatrix} \quad (2.57)$$

We can compute the production rates when the two reaction rates are

$$\begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \end{bmatrix}$$

and we obtain

$$\mathbf{R} = \begin{bmatrix} -2 & 3 & 2 & -3 & -1 & 1 \end{bmatrix}^T \quad (2.58)$$

Now if  $\mathbf{R}$  is determined by measuring species concentrations, unmodeled effects undoubtedly cause discrepancy between predicted and measured values of  $\mathbf{R}$ . For example, let's assume that the production rate of the first species, H, is in error by a small amount so the measured  $\mathbf{R}$  is  $\mathbf{R} = \begin{bmatrix} -2.1 & 3 & 2 & -3 & -1 & 1 \end{bmatrix}^T$ . The effect of this error is to make the equations inconsistent, so there no longer is an exact solution for the reaction rates, which is not too surprising because we have six equations and only two unknowns in Equation 2.57. A system with more equations than unknowns is called over-determined. Normally we would not expect to find a solution for arbitrary  $\mathbf{R}$ , only those  $\mathbf{R}$  that are generated by multiplying an  $\mathbf{r}$  by  $\mathbf{v}^T$ . When the equations are inconsistent, one is usually interested in knowing the values of the two reaction rates that come *closest* to satisfying the six equations simultaneously. If we measure how close the equations are to zero by squaring the error in each equation and summing over all equations, then we are using the classic least-squares approach.

Computing least-squares solutions to over-determined equations is a useful computation in linear algebra. If one is given  $\mathbf{R}$  and trying to solve for  $\mathbf{r}$  from

$$\mathbf{R} = \mathbf{v}^T \mathbf{r} \quad (2.59)$$

then the least-squares solution is given by

$$\mathbf{r} = (\mathbf{v} \mathbf{v}^T)^{-1} \mathbf{v} \mathbf{R}$$

in which the superscript  $-1$  indicates a matrix inverse. If the reactions are linearly independent, then the matrix product  $\mathbf{v} \mathbf{v}^T$  has an inverse and the least-squares solution is unique. If the reactions are not linearly independent this inverse does not exist and the least-squares solution is not unique as before.

If we compute the least-squares solution to the inconsistent data given above, we find  $\mathbf{r} = [0.983 \quad 2.03]^T$  instead of the *correct* value  $\mathbf{r} = [1 \quad 2]^T$ . Notice a small error in the H production rate has translated into small errors in both inferred reaction rates.

As a final example, let's consider the case in which we have repeated measurements of the production rates, all of which are subject to small random errors. If we add small amounts of random noise to the data given in Equation 2.58, we produce the following six measurements.

$$\mathbf{R}_{\text{meas}} = \begin{bmatrix} -2.05 & -2.06 & -1.93 & -1.97 & -2.04 & -1.92 \\ 2.94 & 3.02 & 3.04 & 2.93 & 3.06 & 3.04 \\ 2.01 & 1.94 & 2.01 & 1.92 & 2.01 & 2.04 \\ -2.98 & -2.98 & -2.98 & -2.99 & -2.96 & -2.96 \\ -1.03 & -1.03 & -0.98 & -1.07 & -0.95 & -1.08 \\ 0.97 & 1.05 & 1.06 & 1.09 & 1.00 & 1.07 \end{bmatrix}$$

If we take each column of  $\mathbf{R}_{\text{meas}}$ , that is each production-rate measurement, and compute the least-squares estimate of  $\mathbf{r}$  for that measurement, we obtain six estimates of the reaction rates, one for each measured production rate. We can perform these operations in one matrix equation via

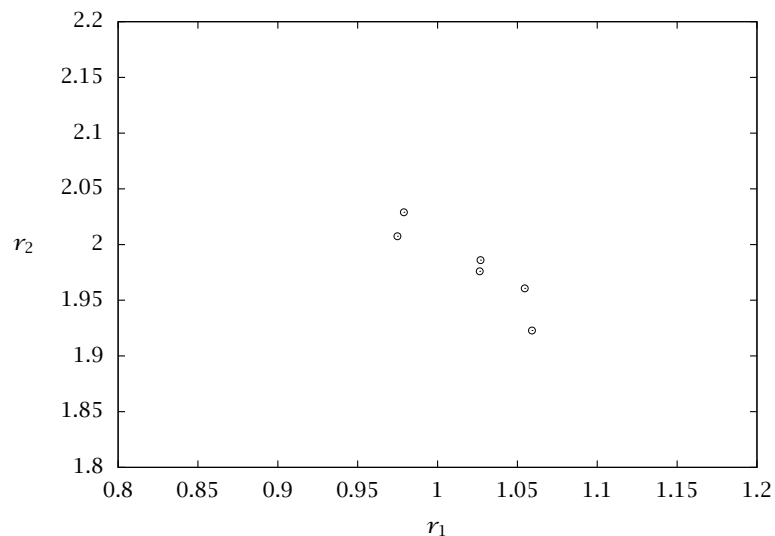
$$\mathbf{r}_{\text{est}} = (\mathbf{v} \mathbf{v}^T)^{-1} \mathbf{v} \mathbf{R}_{\text{meas}}$$

and the result is

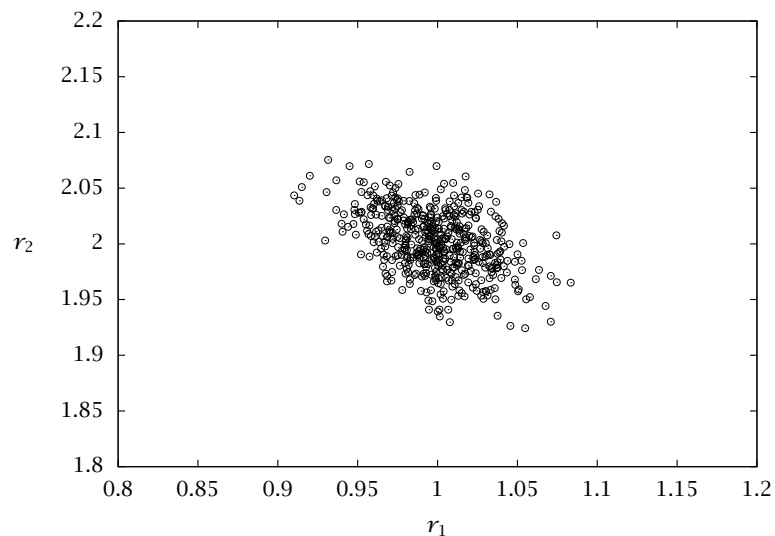
$$\mathbf{r}_{\text{est}} = \begin{bmatrix} 0.97 & 1.03 & 1.03 & 1.06 & 0.98 & 1.05 \\ 2.01 & 1.99 & 1.98 & 1.92 & 2.03 & 1.96 \end{bmatrix}$$

Figure 2.2 shows the estimated reaction rates for the six production-rate measurements. Notice that we obtain reasonable estimates of the true reaction rates,  $\mathbf{r} = [1 \quad 2]^T$ . Next consider what happens when we have many measurements available. Figure 2.3 displays the estimated reaction rates given 500 production-rate measurements. Notice that the estimated rates are again scattered about the true value, the





**Figure 2.2:** Estimated reaction rates from six production-rate measurements subject to measurement noise.



**Figure 2.3:** Estimated reaction rates from 500 production-rate measurements subject to measurement noise.

mean of these values is close to the true value, and the shape of the frequency distribution for the reaction rate estimates begins to emerge. You might want to generate the same plot with 5000 random measurements and see how much more detail is apparent in the probability distribution of estimates. Further discussion of parameter estimation from data is delayed until Chapter 9, but engineers benefit from thinking about extracting information from data and models at an early stage.

## 2.6 Summary

In this chapter we have introduced the compact notation for keeping track of the stoichiometry of chemical reactions,

$$\sum_{j=1}^{n_s} \nu_{ij} A_j = 0, \quad i = 1, 2, \dots, n_r$$

in which  $A_j$  represents chemical species  $j$ ,  $j = 1, \dots, n_s$  and  $n_s$  is the number of species in the reaction network. The stoichiometric coefficients are contained in the stoichiometric matrix  $\mathbf{v}$ , in which  $\nu_{ij}$  is the stoichiometric coefficient for species  $j$  in reaction  $i$ ,  $i = 1, \dots, n_r$  and  $n_r$  is the number of reactions in the network. We can summarize the reaction stoichiometry with one vector equation

$$\mathbf{v}\mathbf{A} = \mathbf{0}$$

A set of reactions is linearly independent if no reaction in the set can be written as a linear combination of the other reactions in the set. Linear independence of reactions is equivalent to linear independence of the rows of  $\mathbf{v}$ . The rank of a matrix is the number of linearly independent rows (equivalently columns) of the matrix, so the rank of  $\mathbf{v}$  is the number of linearly independent reactions in the network.

The reaction rate is a fundamental concept that allows quantitative prediction of rates of conversions of reactants to products. We define the rate of reaction  $i$ ,  $r_i$ , to be the net number of times a reaction event occurs per time per volume. Given the rates of all reactions, we can calculate directly the production rates of all species,

$$R_j = \sum_{i=1}^{n_r} \nu_{ij} r_i, \quad j = 1, \dots, n_s$$

or as an equivalent vector equation,

$$\mathbf{R} = \mathbf{v}^T \mathbf{r} \quad (2.60)$$

Given the rates of reactions, it is a simple matter to compute the species production rates with Equation 2.60. One cannot solve uniquely the reverse problem, in general. Given observed production rates, computing the corresponding reaction rates requires additional information, such as rate expressions for the elementary reactions in a reaction mechanism. If the set of chemical reactions is linearly independent, then one can uniquely solve the reverse problem. If the observed production rates contain experimental errors, there may not exist an exact solution of reaction rates,  $\mathbf{r}$ , that satisfy Equation 2.60. In this situation, one is normally interested in finding the reaction rates that *most closely* satisfy Equation 2.60. The closest solution in a least-squares sense is easily computed with standard linear algebra software.

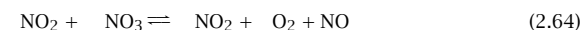
## Notation

$a_{jl}$	formula number for element $l$ in species $j$
$A_j$	$j$ th species in the reaction network
$E^l$	$l$ th element comprising the species
$i$	reaction index, $i = 1, 2, \dots, n_r$
$j$	species index, $j = 1, 2, \dots, n_s$
$M_j$	molecular weight of the $j$ th species
$n_i$	number of independent reactions in reaction network
$n_r$	total number of reactions in reaction network
$n_s$	total number of species in reaction network
$r_i$	reaction rate for $i$ th reaction
$R_j$	production rate for $j$ th species
$\varepsilon_i$	extent of reaction $i$
$v_{ij}$	stoichiometric number for the $j$ th species in the $i$ th reaction

## 2.7 Exercises

### Exercise 2.1: Finding independent sets of reactions

Consider the following set of chemical reactions,



- (a) Determine the stoichiometric matrix,  $\mathbf{v}$ , and the species list,  $\mathbf{A}$ , for this reaction system so the reaction network is summarized by

$$\mathbf{v}\mathbf{A} = \mathbf{0}$$

- (b) Use Octave, MATLAB, or your favorite software package to determine the rank of the stoichiometric matrix. How many of the reactions are linearly independent?
- (c) Now that you have found the number of independent reactions,  $n_i$ , which  $n_i$  of the original set of 6 reactions can be chosen as an independent set? Try guessing some set of  $n_i$  reactions and determine the rank of the new stoichiometric matrix. Stop when you have determined successfully one or more sets of  $n_i$  independent reactions.

Hint: you want to examine the rank of sub-matrices obtained by deleting rows (i.e., reactions) from the original stoichiometric matrix. In Octave, if you assign the original stoichiometric matrix to a name, `stoi`, then you can obtain the rank of the stoichiometric matrix associated with deleting the fifth reaction, for example, by

```
stoi2 = [stoi(1:4,:);stoi(6,:)]
rank(stoi2)
```

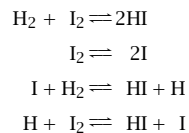
Do you see how the indices in forming `stoi2` work out? Notice we do not have to enter any more matrices after we build the original stoichiometric matrix to test the ranks of various reaction networks.

- (d) What do you think of a colleague's answer that contains Reactions 2.62 and 2.63 in the final set. Can this be correct? Why or why not?

### Exercise 2.2: The stoichiometric matrix

- (a) What is the stoichiometric matrix for the following reaction network [2]? By inspection, how many of the reactions are linearly independent? How would

you check your answer if you had access to a computer?



- (b) Given a stoichiometric matrix for a reaction network with  $n_s$  species and  $n_r$  reactions

$$\sum_{j=1}^{n_s} \nu_{ij} A_j = 0, \quad i = 1, 2, \dots, n_r$$

What is the production rate of the  $j$ th species,  $R_j$ , in terms of the reaction rates for the reactions,  $r_i$ ?

### Exercise 2.3: Finding reaction rates from production rates

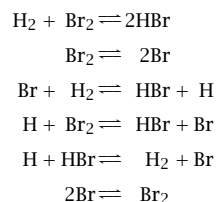
Consider again the water gas shift reaction presented in Equation 2.51. Assume the production rates have been measured and are, in some units of moles/(time·volume),

$$\begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} -1 \\ 3 \\ 1 \\ -3 \\ -2 \\ 2 \end{bmatrix}$$

- (a) If you choose the first two reactions as a linearly independent set, what are the two reaction rates that are consistent with these data. Is this answer unique?
- (b) Repeat the calculation if you choose the second and third reactions as the linearly independent set of reactions. Is this answer unique?
- (c) How can these reaction rates differ, when the production rates are the same? Can we determine which set of reactions is really causing this measured production rate?

### Exercise 2.4: Independent reactions for bromine hydrogenation

Consider the following set of chemical reactions [4, 5],



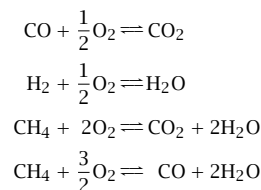
- (a) Determine the stoichiometric matrix,  $\mathbf{v}$ , and the species list,  $\mathbf{A}$ , for this reaction system so the reaction network is summarized by

$$\mathbf{vA} = \mathbf{0}$$

- (b) Use Octave or MATLAB to determine the rank of the matrix using the rank function. How many reactions are linearly independent?
- (c) Now that you have found the number of independent reactions,  $n_i$ , which  $n_i$  of the original set of six reactions can be chosen as an independent set? Try guessing some set of  $n_i$  reactions and determine the rank of the new stoichiometric matrix. Stop when you have determined successfully one or more sets of  $n_i$  independent reactions.

### Exercise 2.5: Independent reactions for methane oxidation

Consider a mixture of CO, H<sub>2</sub>, and CH<sub>4</sub> that is fed into a furnace with O<sub>2</sub> and produces CO, CO<sub>2</sub>, and H<sub>2</sub>O. The following chemical reactions have been suggested to account for the products that form.



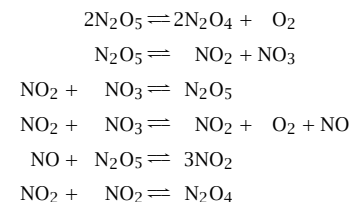
- (a) Are these reactions linearly independent? What is the number of linearly independent reactions,  $n_i$ ?
- (b) List all sets of  $n_i$  linearly independent reactions. Which reaction is included in all of the linearly independent sets of reactions? Why?

### Exercise 2.6: Methane oxidation and maximal independent sets

- (a) List a maximal set of linearly independent reactions if O<sub>2</sub> as well as C are not observed as species in the methane oxidation reactions in Example 2.7.
- (b) Repeat if H<sub>2</sub>, O<sub>2</sub> and C are not observed as species.

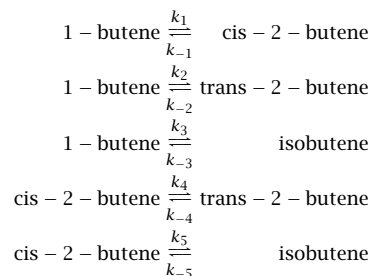
### Exercise 2.7: Production rates from reaction rates

- (a) Consider the following set of chemical reactions,



Determine the rates of production of each component in terms of the rates of each reaction.

(b) Butene isomerization reactions are shown below.



Determine the rates of production of each component in terms of the rates of each reaction.

### Exercise 2.8: Restrictions from element balancing

Let the  $s$  species,  $A_j, j = 1, \dots, s$  be comprised of the  $e$  elements,  $E^l, l = 1, \dots, e$ . Writing the chemical formulas for the species in the usual way

$$\begin{aligned}
 A_1 &= E_{a_{11}}^1 E_{a_{12}}^2 \cdots E_{a_{1e}}^e \\
 A_2 &= E_{a_{21}}^1 E_{a_{22}}^2 \cdots E_{a_{2e}}^e \\
 &\vdots \\
 A_s &= E_{a_{s1}}^1 E_{a_{s2}}^2 \cdots E_{a_{se}}^e
 \end{aligned}$$

in which  $a_{jl}$  is the formula number for species  $j$  corresponding to element  $l$ . Show that any chemical reaction,  $\sum_j \nu_j A_j = 0$  satisfies the following  $e$  equations to balance the elements

$$\begin{bmatrix} \nu_1 & \nu_2 & \cdots & \nu_s \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1e} \\ a_{21} & a_{22} & \cdots & a_{2e} \\ \vdots & \vdots & \ddots & \vdots \\ a_{s1} & a_{s2} & \cdots & a_{se} \end{bmatrix} = \begin{bmatrix} 0 & 0 & \cdots & 0 \end{bmatrix}$$

If we define the  $s \times e$  matrix  $\mathcal{A}$  to hold the formula numbers, we can express the element balance by

$$\nu \mathcal{A} = \mathbf{0} \quad (2.67)$$

Determine  $\mathbf{A}$ ,  $\mathbf{E}$  and  $\mathcal{A}$  for the species hydrogen (molecular), oxygen (molecular) and water.

### Exercise 2.9: Null space and fundamental theorem of linear algebra

Equation 2.67 in Exercise 2.8 is begging to be analyzed by the fundamental theorem of linear algebra [7], so we explore that concept here. Consider an arbitrary  $m \times n$  matrix,  $\mathbf{B}$ . The null space of matrix  $\mathbf{B}$ , written  $\mathcal{N}(\mathbf{B})$ , is defined to be the set of *all* vectors  $\mathbf{x}$  such that  $\mathbf{B} \mathbf{x} = \mathbf{0}$ . The dimension of  $\mathcal{N}(\mathbf{B})$  is the number of linearly independent

vectors  $\mathbf{x}$  satisfying  $\mathbf{B} \mathbf{x} = \mathbf{0}$ . One of the remarkable results of the fundamental theorem of linear algebra is the relation

$$\text{rank}(\mathbf{B}) + \dim(\mathcal{N}(\mathbf{B})) = n$$

The numerical support for computing null spaces is excellent. For example, the Octave command `null(B)` returns a matrix with columns consisting of linearly independent vectors in the null space of matrix  $\mathbf{B}$ .

(a) Armed with this result, consider Equation 2.67 and establish that the number of linearly independent reactions that satisfy the element balances is

$$i = s - \text{rank}(\mathcal{A})$$

(b) Determine  $\mathbf{A}$ ,  $\mathbf{E}$  and  $\mathcal{A}$  for the methane oxidation in Example 2.7.

(c) Determine  $\text{rank}(\mathcal{A})$  and  $i$  for this example. Do you obtain the same size maximal set as in Example 2.7?

### Exercise 2.10: Limits on numbers of independent reactions

(a) Species A, B and C are observed in a reacting system. What is the largest possible number of linearly independent reactions among these species,  $n_{\max}$ ?

(b) What is the smallest possible number,  $n_{\min}$ ?

(c) List a chemical example that has a maximal set with  $n$  reactions for each  $n$  in  $n_{\min} \leq n \leq n_{\max}$ .

### Exercise 2.11: Generating possible independent reaction sets

(a) If one has  $s$  species comprised of  $e$  elements, what are the largest and smallest numbers of linearly independent reactions that can be written among the  $s$  species? Give an example with more than one species in which you cannot write any reactions.

(b) If  $s > e$ , the usual case, how many reactions can be written? Prove you can write at least one valid reaction, or find a counterexample to this statement.

### Exercise 2.12: An alchemist's view of stoichiometry

In the early 1700s, the alchemists were unaware of the defining role that electrons played in bond formation and transformation of chemical species. The structure of the nucleus, elucidation of bond formation with electron sharing and the construction of the periodic table were major triumphs of the chemical and physical sciences in the nineteenth and early twentieth centuries [6, pp.113–166]. Before these developments, chemical transformation of the elements themselves, such as lead to gold, was on the table as an early goal of research.

Imagine a more flexible chemical world in which we demand conservation of *only* mass for a valid chemical reaction; any mass-conserving rearrangements of the protons and neutrons in the nuclei are also considered valid chemical reactions.

Assume we observe  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  as chemical species.

(a) Write a few *mass-conserving* reactions among these species that are not valid chemical reactions.

- (b) How many linearly independent mass-conserving reactions can be constructed? You may want to use the result of Example 2.5 and the idea of the null space introduced in Exercise 2.9 to be sure you have accounted for all linearly independent reactions.
- (c) If you enforce the stronger condition of element balancing, then, by inspection, how many linearly independent valid chemical reactions are possible?

### Exercise 2.13: Generalizing independent reactions

Consider  $s$  species comprised of  $e$  elements, in which  $c$  of the species are chemical compounds, i.e., not pure elements. Let  $i$  be the number of reactions in the maximal independent set. Show

$$\max(0, s - e) \leq i \leq \min(s - 1, c)$$

Hint: use the result  $i = s - \text{rank}(\mathcal{A})$  from Exercise 2.9 and determine upper and lower bounds on the rank of  $\mathcal{A}$  based on  $s$ ,  $e$  and  $c$ .

### Exercise 2.14: Eliminating reaction intermediates

Consider the following reaction mechanism with five reactions and eight species, A-H.



and assume that species B, C, and F are highly reactive intermediates.

- (a) What is the maximum number of linearly independent linear combinations of these five reactions that do not contain species B, C, and F as reactants or products. Justify your answer.
- (b) List one set of these independent reactions that contains only small, integer-valued stoichiometric coefficients.

### Exercise 2.15: Reaction rates from production rates

Consider the two reactions



The following production rates were observed in the laboratory for this mechanism:

$$R_A = -4.0 \text{ mol}/(\text{time vol}) \quad R_B = 2.2 \text{ mol}/(\text{time vol}) \quad R_C = 1.0 \text{ mol}/(\text{time vol})$$

- (a) From these measurements, provide a least-squares estimate of the two reaction rates. Recall the least-squares estimate formula is

$$\mathbf{r}_{\text{est}} = (\mathbf{v} \mathbf{v}^T)^{-1} \mathbf{v} \mathbf{R}_{\text{meas}}$$

- (b) Write out the production rates for all the species in terms of the two reaction rates.

- (c) Calculate the three production rates using the estimated reaction rates. Compare this result to the measured production rates. Comment on why the two sets of production rates are or are not different from each other.

We should point out that these limits on numbers of reactions in Exercises 2.8–2.13 presume that conserving elements in the chemical reactions is the *only* restriction. If other quantities are conserved, the method of analysis remains valid, but the answers change. We will see one such conserved quantity, the surface site, when we study reactions with catalytic surfaces in Chapter 5.

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