Stoichioimetry of Chemical Reactions*

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1 Chemical Reactions and Stoichiometry

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

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \tag{1}$$

The rate of this reaction is important in determining the CO/CO_2 ratio in exhaust gases from internal combustion engines, and in determining the H_2 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,

$$H_2O + H \rightleftharpoons H_2 + OH \tag{2}$$

$$OH + CO \rightleftharpoons CO_2 + H \tag{3}$$

Reactions 1–3 comprise a simple reaction network. There are three chemical reactions and six different chemical species taking part in the three reactions, H, H_2, OH, H_2O, CO, and CO_2.

In order to organize the way we discuss chemical reactions, the following notation is convenient. Let the symbol, A_j, represent the jth species taking part in a reaction. In the first example, we can choose $A_1 = NO$, $A_2 = O_2$, and $A_3 = NO_2$. In the water gas shift example, we can choose $A_1 = H$, $A_2 = H_2$, $A_3 = OH$, $A_4 = H_2O$, $A_5 = CO$, and $A_6 = CO_2$.

*Parts of these notes are taken from Rawlings and Ekerdt (2012)

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Using the A_j notation, we can express the water gas shift reactions as

$$\begin{array}{ccccccc} A_4 & + & A_5 & \rightleftharpoons & A_6 & + & A_2 \\ A_4 & + & A_1 & \rightleftharpoons & A_2 & + & A_3 \\ A_3 & + & A_5 & \rightleftharpoons & A_6 & + & A_1 \end{array} \tag{4}$$

Reactions 4 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,

$$\begin{aligned} -A_4 - A_5 + A_6 + A_2 &= 0 \\ -A_4 - A_1 + A_2 + A_3 &= 0 \\ -A_3 - A_5 + A_6 + A_1 &= 0 \end{aligned} \tag{5}$$

Again notice the sign convention that **p***roducts* have **p***ositive* coefficients and *reactants* have *negative* coefficients in Equations 5.[1] Equations 5 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 5 as

$$\begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \tag{6}$$

The matrix appearing in Equation 6 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 $\boldsymbol{\nu}$, and writing $\boldsymbol{A}$ to denote the column vector of the A_j, $j = 1, \ldots, 6$, our final summary of the water gas shift reaction appears as

$$\boldsymbol{\nu A} = \boldsymbol{0}$$

The element ν_{ij} in the stoichiometric matrix is the stoichiometric coefficient for the jth species in the ith 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 $\boldsymbol{\nu}$ 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.

[1] Boldface letters provide a mnemonic device.

Example 1: Stoichiometric matrix for a single reaction

Find the stoichiometric matrix for the nitric oxide example,

$$2NO + O_2 \rightleftharpoons 2NO_2$$

Solution

The nitric oxide example consists of one reaction and three species. We can assign the species to the $\boldsymbol{A}$ as follows: $A_1 = NO$, $A_2 = O_2$, $A_3 = NO_2$. 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,

$$\boldsymbol{\nu} = \begin{bmatrix} -2 & -1 & 2 \end{bmatrix}$$

□

2 Independent Reactions

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

$$\begin{aligned} H_2O + CO &\rightleftharpoons CO_2 + H_2 \\ H_2O + H &\rightleftharpoons H_2 + OH \\ OH + CO &\rightleftharpoons CO_2 + H \end{aligned} \tag{7}$$

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 7 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.

$$\begin{array}{rccccccc} & H_2O & + & \boxed{H} & \rightleftharpoons & H_2 & + & \boxed{OH} \\ + & \boxed{OH} & + & CO & \rightleftharpoons & CO_2 & + & \boxed{H} \\ \hline & H_2O & + & CO & \rightleftharpoons & CO_2 & + & H_2 \end{array}$$

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

$$H_2O + H \rightleftharpoons H_2 + OH \tag{8}$$
$$OH + CO \rightleftharpoons CO_2 + H \tag{9}$$

The answer is now yes, because no multiple of Reaction 8 can equal Reaction 9. There is no way to produce CO or CO_2 from only Reaction 8. Likewise there is no way to produce H_2 or H_2O from only Reaction 9.

This discussion is *not* meant to imply that there is something *wrong* with the first reaction in Reactions 7. 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.

$$\begin{array}{cccccccc} & H_2O & + & \boxed{CO} & \rightleftharpoons & \boxed{CO_2} & + & H_2 \\ - & \{\, OH & + & \boxed{CO} & \rightleftharpoons & \boxed{CO_2} & + & H \,\} \\ \hline & H_2O & + & H & \rightleftharpoons & H_2 & + & OH \end{array}$$

So the first and third reactions could be chosen as the independent set of two reactions. Finally, the third reaction in Reaction 7 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 6

$$\boldsymbol{\nu} = \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \tag{10}$$

We can make an important mathematical connection to the preceding physical arguments. The question of whether or not the ith *reaction* can be written as a linear combination of the other reactions is the same as the question of whether or not the ith *row* of the $\boldsymbol{\nu}$ 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

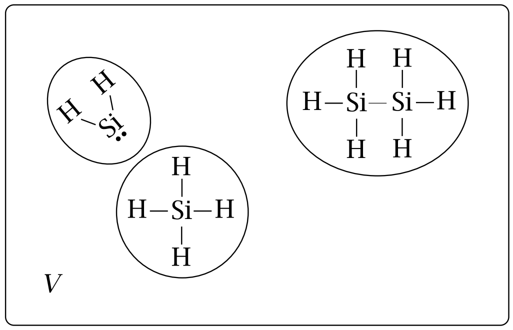

Figure 1: Defining the reaction rate, r, for the reaction $SiH_2 + SiH_4 \rightleftharpoons Si_2H_6$.

a network, n_i, is equal to the rank of $\boldsymbol{\nu}$. 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 Strang (1980) or another linear algebra text for a lucid explanation of the algorithm, Gaussian elimination with partial pivoting.

3 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 following reaction in CVD chemistry

$$SiH_4 + SiH_2 \rightleftharpoons Si_2H_6 \tag{11}$$

The **reaction rate**, r, is defined as the number of times this reaction event takes place per time per volume. One can imagine turning SiH_4, SiH_2 and Si_2H_6 molecules loose in a box of some fixed volume V as depicted in Figure 1. We define the **reaction extent**, ε, 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 SiH_4 molecule hit an SiH_2 molecule and turned into an Si_2H_6 molecule during a short period of time. The change in the reaction extent, $\Delta\varepsilon$, is the net number of reaction events that occur in the time interval Δt. The reaction rate is then

$$r = \frac{\Delta\varepsilon}{\Delta t V} \tag{12}$$

If the forward event (an SiH_4 molecule and an SiH_2 molecule turning into an Si_2H_6 molecule) occurs more often than the reverse event (an Si_2H_6 molecule decomposing into an SiH_4 molecule and an SiH_2 molecule), then the change in ε is positive and the reaction rate is positive. If the reverse event occurs more often than the forward event, then the change in ε and reaction rate are negative. If the system is at equilibrium, then the change in ε is zero and the forward and reverse events occur in equal numbers. The extent ε is a number of molecular change events and therefore the units of r in Equation 12 are #/(time·volume). If one divides by Avogadro's number, the units of extent are moles and the units of reaction rate are moles/(time·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**.

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 jth species is produced (moles/(time·volume)) due to the chemical reactions taking place. It is clear looking at the stoichiometry in Reaction 11 that each time the forward reaction event occurs, an Si_2H_6 molecule is produced. Each time the reverse reaction occurs, an Si_2H_6 molecule is consumed. The production rate of Si_2H_6, $R_{Si_2H_6}$, is therefore directly related to the reaction rate,

$$R_{Si_2H_6} = r$$

Notice that if r is positive $R_{Si_2H_6}$ is positive as we expect because Si_2H_6 is being produced. Similar arguments lead to relating the other production rates to the reaction rate,

$$\begin{aligned} R_{SiH_4} &= -r \\ R_{SiH_2} &= -r \end{aligned}$$

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, $\boldsymbol{R}$,

$$\boldsymbol{R} = \begin{bmatrix} R_{SiH_4} \\ R_{SiH_2} \\ R_{Si_2H_6} \end{bmatrix}$$

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

$$\boldsymbol{R} = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix} r \tag{13}$$

Notice that the column vector in Equation 13 is just the transpose of the row vector that comprises $\boldsymbol{\nu} = [-1 \;\; -1 \;\; 1]$, which follows from Reaction 11

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,

$$
\begin{aligned}
H_2O + CO &\rightleftharpoons CO_2 + H_2 \\
H_2O + H &\rightleftharpoons H_2 + OH \\
OH + CO &\rightleftharpoons CO_2 + H
\end{aligned}
$$

Three reaction rates are required to track all three reactions. Let r_i denote the reaction rate for the ith 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

$$R_H = (0)\, r_1 + (-1)\, r_2 + (1)\, r_3 = -r_2 + r_3$$

Consider the second species, H_2. It is produced in the first and second reactions and does not take part in the third reaction. Its productionrate can therefore be expressed as

$$R_{H_2} = (1)\, r_1 + (1)\, r_2 + (0)\, r_3 = r_1 + r_2$$

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

$$
\begin{bmatrix} R_H \\ R_{H_2} \\ R_{OH} \\ R_{H_2O} \\ R_{CO} \\ R_{CO_2} \end{bmatrix}
=
\begin{bmatrix} 0 & -1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \\ -1 & -1 & 0 \\ -1 & 0 & -1 \\ 1 & 0 & 1 \end{bmatrix}
\begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix}
\qquad (14)
$$

The fundamental relationship between the reaction rates and the production rates now emerges. Compare the matrices in Equations 6 and 14. Notice that the first *row* of the matrix in Equation 6 is the same as the first *column* of the matrix in Equation 14. Moreover, *each* row of the matrix in Equation 6 is the same as the corresponding column of the matrix in Equation 14. In other words, the two matrices are transposes of each other. We can therefore summarize Equation 14 as

$$\boxed{\boldsymbol{R} = \boldsymbol{\nu}^T \boldsymbol{r}} \qquad (15)$$

in which $\boldsymbol{\nu}^T$ denotes the transpose of the stoichiometric matrix. Equation 15 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.

Notation

a_{jl}	formula number for element l in species j
A_j	jth species in the reaction network
E^l	lth element comprising the species
i	reaction index, $i = 1, 2, \ldots, n_r$
j	species index, $j = 1, 2, \ldots, n_s$
M_j	molecular weight of the jth 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 ith reaction
R_j	production rate for jth species
ε_i	extent of reaction i
ν_{ij}	stoichiometric number for the jth species in the ith reaction

4 Exercises

Exercise 1: Finding independent sets of reactions

Consider the following set of chemical reactions,

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2 \tag{16}$$
$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \tag{17}$$
$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \tag{18}$$
$$NO_2 + NO_3 \rightleftharpoons NO_2 + O_2 + NO \tag{19}$$
$$NO + N_2O_5 \rightleftharpoons 3NO_2 \tag{20}$$
$$NO_2 + NO_2 \rightleftharpoons N_2O_4 \tag{21}$$

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

$$\boldsymbol{\nu A} = \boldsymbol{0}$$

(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 17 and 18 in the final set. Can this be correct? Why or why not?

Exercise 2: The stoichiometric matrix

(a) What is the stoichiometric matrix for the following reaction network Benson and Srinivasan (1955)? By inspection, how many of the reactions are linearly independent? How would you check your answer if you had access to a computer?

$$\begin{aligned} H_2 + I_2 &\rightleftharpoons 2HI \\ I_2 &\rightleftharpoons 2I \\ I + H_2 &\rightleftharpoons HI + H \\ H + I_2 &\rightleftharpoons HI + I \end{aligned}$$

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

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

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

Exercise 3: Finding reaction rates from production rates

Consider again the water gas shift reaction presented in Reactions 1–3. Assume the production rates have been measured and are, in some units of moles/(time·volume),

$$\begin{bmatrix} R_{H} \\ R_{H_2} \\ R_{OH} \\ R_{H_2O} \\ R_{CO} \\ R_{CO_2} \end{bmatrix} = \begin{bmatrix} -1 \\ 3 \\ 1 \\ -3 \\ -2 \\ 2 \end{bmatrix}$$

(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 4: Independent reactions for bromine hydrogenation

Consider the following set of chemical reactions Herzfeld (1919); Polanyi (1920),

$$\begin{aligned} H_2 + Br_2 &\rightleftharpoons 2HBr \\ Br_2 &\rightleftharpoons 2Br \\ Br + H_2 &\rightleftharpoons HBr + H \\ H + Br_2 &\rightleftharpoons HBr + Br \\ H + HBr &\rightleftharpoons H_2 + Br \\ 2Br &\rightleftharpoons Br_2 \end{aligned}$$

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

$$\boldsymbol{\nu A} = \boldsymbol{0}$$

(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 5: Independent reactions for methane oxidation

Consider a mixture of CO, H_2, and CH_4 that is fed into a furnace with O_2 and produces CO, CO_2, and H_2O. The following chemical reactions have been suggested to account for the products that form.

$$
\begin{aligned}
CO + \frac{1}{2}O_2 &\rightleftharpoons CO_2 \\
H_2 + \frac{1}{2}O_2 &\rightleftharpoons H_2O \\
CH_4 + 2O_2 &\rightleftharpoons CO_2 + 2H_2O \\
CH_4 + \frac{3}{2}O_2 &\rightleftharpoons CO + 2H_2O
\end{aligned}
$$

(a) Are these reactions linearly independent? How many reactions comprise a linearly independent set?

(b) List all sets of linearly independent reactions. Which reaction is included in all of the linearly independent sets of reactions? Why?

Exercise 6: Production rates from reaction rates

(a) Consider the following set of chemical reactions,

$$
\begin{aligned}
2N_2O_5 &\rightleftharpoons 2N_2O_4 + O_2 \\
N_2O_5 &\rightleftharpoons NO_2 + NO_3 \\
NO_2 + NO_3 &\rightleftharpoons N_2O_5 \\
NO_2 + NO_3 &\rightleftharpoons NO_2 + O_2 + NO \\
NO + N_2O_5 &\rightleftharpoons 3NO_2 \\
NO_2 + NO_2 &\rightleftharpoons N_2O_4
\end{aligned}
$$

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

(b) Butene isomerization reactions are shown below.

$$1-\text{butene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{cis}-2-\text{butene}$$
$$1-\text{butene} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{trans}-2-\text{butene}$$
$$1-\text{butene} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{isobutene}$$
$$\text{cis}-2-\text{butene} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{trans}-2-\text{butene}$$
$$\text{cis}-2-\text{butene} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{isobutene}$$

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

Exercise 7: Eliminating reaction intermediates

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

$$A \longrightarrow B + C \qquad (22)$$
$$C \longrightarrow B + D \qquad (23)$$
$$A + B \longrightarrow E + F \qquad (24)$$
$$F \longrightarrow G + B \qquad (25)$$
$$B + F \longrightarrow H \qquad (26)$$

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 8: Stoichiometry short questions

(a) What is the difference between a set of reactions that is linearly independent and a set of reactions that is linearly dependent?

(b) For the reaction

$$2NO + O_2 \rightleftharpoons 2NO_2$$

is it likely that this overall reaction would occur also as a molecular event? Why or why not?

(c) Consider the set of reactions

$$\begin{aligned} A + B + 2C &\rightleftharpoons D + E \\ A &\rightleftharpoons B + E \\ 2B + 2C &\rightleftharpoons D \end{aligned}$$

1. Write out the species list and stoichiometric matrix. For ease of grading, please keep the species in alphabetical order in the species list.
2. By inspection, what is the rank of this matrix? Explain your answer.

Exercise 9: Reaction rates from production rates

Consider the two reactions

$$\begin{aligned} A &\rightleftharpoons B \\ 2B &\rightleftharpoons C \end{aligned}$$

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

$$R_A = -4.5 \text{ mol/(time vol)} \qquad R_B = 2.2 \text{ mol/(time vol)} \qquad R_C = 0.5 \text{ mol/(time vol)}$$

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

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

(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.

Exercise 10: Least squares estimate for multiple measurements

Consider again the water gas shift reaction presented in Reactions 1–3. Consider the first two reactions as a linearly independent set.

$$\begin{aligned} H_2O + CO &\rightleftharpoons CO_2 + H_2 \\ H_2O + H &\rightleftharpoons H_2 + OH \end{aligned}$$

We are provided with the following six replicate experimental measurements of the species production rates, all of which are subject to small measurement errors.

$$\boldsymbol{R}_{\text{meas}} = \begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} -2.05 & -2.06 & -1.93 & -1.97 & -2.04 & -1.92 \\ 2.94 & 3.02 & 3.04 & 2.93 & 3.06 & 3.04 \\ 2.01 & 1.94 & 2.01 & 1.92 & 2.01 & 2.04 \\ -2.98 & -2.98 & -2.98 & -2.99 & -2.96 & -2.96 \\ -1.03 & -1.03 & -0.98 & -1.07 & -0.95 & -1.08 \\ 0.97 & 1.05 & 1.06 & 1.09 & 1.00 & 1.07 \end{bmatrix}$$

(a) Consider each column of $\boldsymbol{R}_{\text{meas}}$, that is each production rate measurement, and compute a least-squares estimate of $\boldsymbol{r}$ for that measurement. Confirm that your six least-squares estimates are:

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

(b) Next consider all six measurements simultaneously. Find one estimate of $\boldsymbol{r}$ that simultaneously minimizes the squared errors of all six of the measured production rates. Confirm that your estimate is

$$\boldsymbol{r}_{\text{est}} = \begin{bmatrix} 1.02 \\ 1.98 \end{bmatrix} \qquad \text{all six measurements considered}$$

Hint: Consider the least squares problem $\boldsymbol{A}\boldsymbol{x} = \boldsymbol{b}$. To create the $\boldsymbol{b}$ vector for this problem, you can manually insert the six $\boldsymbol{R}_{\text{meas}}$ vectors into one column vector, or you may want to try the MATLAB command: `reshape`. To create the $\boldsymbol{A}$ matrix, you can manually insert the stoichiometric matrix six times, or you may want to use the MATLAB command: `repmat` or `kron`. The functions `reshape`, `repmat`, and `kron` are powerful and convenient tools for reorganizing matrices and vectors. See the MATLAB help for their use.

(c) Plot the six single-measurement estimates and the one multiple-measurement estimate with r_1, r_2 as the x-y axes. Where does the multiple-measurement estimate lie with respect to the six single-measurement estimates? Which of the seven estimates available do you think is the most reliable estimate of the two reaction rates and why?

Exercise 11: Don't retype data!

Next consider Exercise 10 with 500 measurements. The measurements are in the file

`lots_of_data.dat`

with the first few measurements shown below

-2.05	-2.06	-1.93	-1.97	-2.04	-1.92	-1.99	-2.00	-2.05
2.94	3.02	3.04	2.93	3.06	3.04	3.00	2.94	3.01
2.01	1.94	2.01	1.92	2.01	2.04	2.06	1.90	1.98
-2.98	-2.98	-2.98	-2.99	-2.96	-2.96	-2.99	-2.96	-2.96
-1.03	-1.03	-0.98	-1.07	-0.95	-1.08	-1.04	-1.01	-1.00
0.97	1.05	1.06	1.09	1.00	1.07	0.98	1.02	1.01

Download the 500 measurements with your browser, save them to a file named `lots_of_data.dat`, and load the data into MATLAB using the `load` command.

```
b = load ('lots_of_data.dat')
```

The matrix of 500 measurements will then be stored in the variable `b`.

(a) Repeat Exercise 10 (a)–(c) on these data.

(b) Describe the pattern of points for the 500 estimates? Do you see any structure to these estimates?

Exercise 12: Writing functions in MATLAB and Octave

Let's do Exercise 11 with a function instead of a script file. Define the following function

```
xls = least_sq(datafile, A)
```

in which `datafile` is the name of a file containing the measurements, and `A` is the A matrix corresponding to the linear model

$$Ax = b$$

Note that variables can be set to names; these variables are called strings. You assign the variable `datafile` to the name of the file containing the data by setting the name inside quotes

```
datafile = 'name_of_file_containing_data'
```

Your function should first load the file `datafile`. Then it should check how many experiments are contained in the file. Assume each column contained in the file is a measurement of b. Then stack the measurements in a column vector, stack the A matrix the appropriate number of times, solve for $\hat{x}$, and return the single estimated value using all of the measurements.

Check your function by writing a short script that calls the function `least_sq` to solve Exercise 11 and check your result against your previous calculation in Exercise 11.

Exercise 13: Functions with multiple return arguments

Let's write a function to do Exercise 1. Use the `nchoosek` function inside your function to make your code as general as possible.

Write a function

```
[indreac, r] = ind_sets(V)
```

in which `V` is a stoichiometric matrix, `r` is its rank r, and `indreac` is a matrix containing the set of all linearly independent reactions, with each row containing a set of r integers corresponding to a set of reactions that are linearly independent. A function can return more than one argument, by placing the list of return arguments inside square brackets as above.

(a) Pass in the stoichiometric matrix from Exercise 1 to check your function. Print out the returned matrix `indreac` for this problem.

(b) Find your own favorite chemical reaction set with 7 or more reactions and species whose rank is at least 2 less than the number of reactions. Apply your function to this stoichiometric matrix and print out the list of all linearly independent reactions.

Notice that when you have a calculation that you need to repeat many times on different data, it's convenient to write and store a function to perform the calculation.

Exercise 14: Estimating reaction rates from production rates — number of measurements

Consider the chemical reactions

$$\begin{aligned} A + B &\longrightarrow C \qquad r_1 \\ C &\longrightarrow D \qquad r_2 \end{aligned}$$

We have measurements of production rates and would like to estimate the corresponding reaction rates.

(a) Assume we can measure A, B, C, and D concentrations. Fifty measurements are available on the class website in this file

`loseinfo.dat`

with the first seven measurements shown below

```
R_A    -7.54   -6.99   -6.88   -7.31   -7.12   -7.39   -7.33
R_B    -7.42   -6.91   -6.90   -6.94   -7.38   -7.32   -6.95
R_C     2.92    2.90    2.91    3.20    3.05    3.36    2.69
R_D     4.23    4.04    4.07    4.17    3.70    4.04    4.25
```

Compute least squares estimates of the reaction rates for each of the 50 measurements. Next compute the single best reaction rate estimate for all 50 measurements. Plot the 50 estimates and the single best estimate for all 50 measurements on one plot.

(b) Assume we are able to measure A, B, and C only. Delete the last row from the measurement matrix and repeat part (14a).

(c) Assume we are able to measure A and B only. Delete the last two rows from the measurement matrix and repeat part (14a).

(d) Compare and contrast the reaction rate estimates for the three sets of measurements (A,B,C,D), (A,B,C) and (A,B). Discuss the effect of removing species measurements on the estimated reaction rates.

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