Stoichiometry: the determination of the proportions in which chemical elements combine or are produced and the weight relations in any chemical reaction.¹

- the stoichiometric matrix, $\nu$
- linearly independent reactions
- mass conservation in chemical reactions
- reaction rates, $r_i$, $i = 1, \ldots, n_r$
- production rates, $R_j$, $j = 1, \ldots, n_s$


Chemical Reactions and Stoichiometry

- Nitric oxide, smog formation in the atmosphere. 1 reaction among 3 species.
- Water-gas shift reaction. 3 reactions among 6 species.
- Chemical vapor deposition. 20 reactions among 14 species.
Nitric Oxide

\[ 2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \]

One chemical reaction and three different chemical species: NO, O₂, and NO₂.

Water-Gas Shift Reaction

\[ \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
\[ \text{H}_2\text{O} + \text{H} \rightleftharpoons \text{H}_2 + \text{OH} \]
\[ \text{OH} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H} \]

Three chemical reactions and six different chemical species: H, H₂, OH, H₂O, CO, and CO₂.
Let \( A_j \) represent the \( j \)th species
\( A_1 = \text{H}, \ A_2 = \text{H}_2, \ A_3 = \text{OH}, \ A_4 = \text{H}_2\text{O}, \ A_5 = \text{CO}, \text{ and } A_6 = \text{CO}_2. \)
Species Vector and Sign Convention

\[
\begin{align*}
\text{H}_2\text{O} + \text{CO} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\text{H}_2\text{O} + \text{H} & \rightleftharpoons \text{H}_2 + \text{OH} \\
\text{OH} + \text{CO} & \rightleftharpoons \text{CO}_2 + \text{H}
\end{align*}
\]

\[A_1 = \text{H}, \ A_2 = \text{H}_2, \ A_3 = \text{OH}, \ A_4 = \text{H}_2\text{O}, \ A_5 = \text{CO}, \text{ and } A_6 = \text{CO}_2.\]

\[
\begin{align*}
A_4 + A_5 & \rightleftharpoons A_6 + A_2 \\
A_4 + A_1 & \rightleftharpoons A_2 + A_3 \\
A_3 + A_5 & \rightleftharpoons A_6 + A_1
\end{align*}
\]

products have positive coefficients
reactants have negative coefficients
The Stoichiometric Matrix

\[
\begin{bmatrix}
0 & 1 & 0 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 & 0 & 0 \\
1 & 0 & -1 & 0 & -1 & 1
\end{bmatrix}
\begin{bmatrix}
A_1 \\
A_2 \\
A_3 \\
A_4 \\
A_5 \\
A_6
\end{bmatrix}
= \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}
\]

(2.7)

stoichiometric matrix \( \nu \)

A column vector of \( A_j \), \( j = 1, \ldots, 6 \)

\( \nu A = 0 \)

---

The \( i \)th reaction and the \( j \)th species

\[
\sum_{j=1}^{n_s} \nu_{ij} A_j = 0, \quad i = 1, \ldots, n_r
\]

\( i \) runs from 1 to \( n_r \), the total number of reactions in the network

\( j \) runs from 1 to \( n_s \), the total number of species in the network
The stoichiometric matrix for a single reaction is a row vector.

\[
\nu = \begin{bmatrix}
-2 \\ -1 \\ 2
\end{bmatrix}
\]

Instead of \(A_1 = H\) and \(A_6 = CO_2\), what is the stoichiometric matrix if \(A_1 = CO_2\) and \(A_6 = H\)?

Modified species vector:

\[
A'_1 = CO_2, \ A'_2 = H_2, \ A'_3 = OH, \ A'_4 = H_2O, \ A'_5 = CO, \ and \ A'_6 = H.
\]
Switching species one and six in the $A$ implies switching the first and sixth columns in the stoichiometric matrix.

Connection of the columns of $\nu$ and the species taking part in the reactions.

The $j$th column of the $\nu$ matrix supplies the stoichiometric numbers of the $j$th species in all of the reactions.
\[
\begin{align*}
H_2O + CO & \rightleftharpoons CO_2 + H_2 \\
H_2O + H & \rightleftharpoons H_2 + OH \\
OH + CO & \rightleftharpoons CO_2 + H
\end{align*}
\]

\(A_1 = H, A_2 = H_2, A_3 = OH, A_4 = H_2O, A_5 = CO, \) and \(A_6 = CO_2.\)

Exchange the first and third reactions

\[
\begin{align*}
OH + CO & \rightleftharpoons CO_2 + H \\
H_2O + H & \rightleftharpoons H_2 + OH \\
H_2O + CO & \rightleftharpoons CO_2 + H
\end{align*}
\]

\[
\nu'' = \begin{bmatrix} 1 & 0 & -1 & 0 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & -1 & 1 \end{bmatrix}
\]
- Exchanging the orders of the first and third reactions causes us to exchange the first and third rows in the \( \nu \) matrix.
- Connection of the rows of \( \nu \) and the reactions.
- The \( i \)th row of the stoichiometric matrix contains the stoichiometric numbers of all species in the \( i \)th reaction.
- 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.

**Silicon chemical vapor deposition (CVD)**

\[
\begin{align*}
\text{SiH}_4 & \overset{\text{SiH}_2 + \text{H}_2} \iff \\
\text{SiH}_4 & \overset{\text{SiH}_3 + \text{H}} \iff \\
\text{SiH}_4 + \text{SiH}_2 & \iff \text{Si}_2\text{H}_6 \\
\text{Si}_2\text{H}_4 + \text{H}_2 & \iff \text{SiH}_4 + \text{SiH}_2 \\
\text{SiH}_4 + \text{H} & \iff \text{SiH}_3 + \text{H}_2 \\
\text{SiH}_4 + \text{SiH}_3 & \iff \text{Si}_2\text{H}_5 + \text{H}_2 \\
\text{SiH}_4 + \text{SiH} & \iff \text{SiH}_3 + \text{SiH}_2 \\
\text{SiH}_4 + \text{Si} & \iff 2\text{SiH}_2 \\
\text{Si} + \text{H}_2 & \iff \text{SiH}_2 \\
\text{SiH}_2 + \text{SiH} & \iff \text{Si}_2\text{H}_3 \\
\text{SiH}_2 + \text{Si} & \iff \text{Si}_2\text{H}_2 \\
\text{SiH}_2 + \text{Si}_3 & \iff \text{Si}_2\text{H}_2 + \text{Si}_2 \\
\text{H}_2 + \text{Si}_2\text{H}_2 & \iff \text{Si}_2\text{H}_4 \\
\text{H}_2 + \text{Si}_2\text{H}_4 & \iff \text{Si}_2\text{H}_6 \\
\text{H}_2 + \text{SiH} & \iff \text{SiH}_3 \\
\text{H}_2 + \text{Si}_2 & \iff \text{Si}_2\text{H}_2 \\
\text{H}_2 + \text{Si}_2\text{H}_3 & \iff \text{Si}_2\text{H}_5 \\
\text{Si}_2\text{H}_2 + \text{H} & \iff \text{Si}_2\text{H}_3 \\
\text{Si} + \text{Si}_3 & \iff 2\text{Si}_2
\end{align*}
\]
The CVD reactions are a simplified version of 120 reactions that were originally postulated for this reaction network [1].

Combustion chemistry: several hundred reactions.

Polymerizations and long-chain-producing reactions: thousands of species and associated reactions.

The stoichiometry of these complex problems is intractable if we do not develop a systematic, automated procedure.

Stoichiometric matrix for CVD chemistry

There are 20 reactions, $n_r = 20$.
There are 14 different species, $n_s = 14$.
A possible assignment to the $A$ vector is: H, H$_2$, Si, SiH, SiH$_2$, SiH$_3$, SiH$_4$, Si$_2$, Si$_2$H$_2$, Si$_2$H$_3$, Si$_2$H$_4$, Si$_2$H$_5$, Si$_2$H$_6$, Si$_3$. 
\[ \nu = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \]

\( \nu \) is a 20 \times 14 matrix; it contains many zero entries. A matrix with many zero entries is called sparse. Physical fact: very few molecules can take part in a particular reaction. Why? All of the reactions in the CVD chemistry are unimolecular or bimolecular.
Show conservation of mass in a chemical reaction can be stated as

\[ \nu M = 0 \]

in which \( M_j \) is the molecular weight of species \( j \).

What is conserved?

\[ 2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \]

- In a chemical reaction, the number of molecules is not conserved
- In a chemical (i.e. not nuclear) reaction, elements are conserved
- In a chemical (i.e. not nuclear) reaction, mass is conserved
Conservation of mass

\[ 2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \]

The molecular weights of reactants and products are related by \(2M_{\text{NO}} + M_{\text{O}_2} = 2M_{\text{NO}_2}\).

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

\(\nu M = 0\)

Conservation of Mass

\[ \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]
\[ \text{H}_2\text{O} + \text{H} \rightleftharpoons \text{H}_2 + \text{OH} \]
\[ \text{OH} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H} \]

\(A_1 = \text{H}, A_2 = \text{H}_2, A_3 = \text{OH}, A_4 = \text{H}_2\text{O}, A_5 = \text{CO}, \text{and } A_6 = \text{CO}_2.\)

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

the superscript \(T\) means the transpose of the matrix.

For the first reaction, \(\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2\), we know

\[ M_{\text{CO}_2} + M_{\text{H}_2} - M_{\text{H}_2\text{O}} - M_{\text{CO}} = 0 \]
### Conservation of Mass

\[
\begin{bmatrix}
0 & 1 & 0 & -1 & -1 & 1
\end{bmatrix}
\begin{bmatrix}
M_H \\
M_{H_2} \\
M_{OH} \\
M_{H_2O} \\
M_{CO} \\
M_{CO_2}
\end{bmatrix} = 0
\]

\[\nu M = 0\]

---

### Independent Reactions

\[H_2O + CO \iff CO_2 + H_2\]

\[H_2O + H \iff H_2 + OH\]

\[OH + CO \iff CO_2 + H\]

**Question:** can we 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. Can we express the first reaction as a linear combination of the second and third reactions?
By inspection, the first reaction is the sum of the second and third reactions, so the set of three reactions is not independent.

\[
\begin{align*}
    \text{H}_2\text{O} &+ \text{H} &\rightleftharpoons & \text{H}_2 &+ \text{OH} \\
    + \text{OH} &+ \text{CO} &\rightleftharpoons & \text{CO}_2 &+ \text{H} \\
    \hline
    \text{H}_2\text{O} &+ \text{CO} &\rightleftharpoons & \text{CO}_2 &+ \text{H}_2
\end{align*}
\]

If we deleted the first reaction from the network, would the remaining two reactions be independent? Why or why not?

\[
\begin{align*}
    \text{H}_2\text{O} + \text{H} &\rightleftharpoons \text{H}_2 + \text{OH} \\
    \text{OH} + \text{CO} &\rightleftharpoons \text{CO}_2 + \text{H}
\end{align*}
\]

There is nothing \textit{wrong} with the first reaction

Can we write the second reaction as a linear combination of the first and third reactions?

\[
\begin{align*}
    \text{H}_2\text{O} &+ \text{CO} &\rightleftharpoons & \text{CO}_2 &+ \text{H}_2 \\
    - \{ \text{OH} &+ \text{CO} &\rightleftharpoons & \text{CO}_2 &+ \text{H} \} \\
    \hline
    \text{H}_2\text{O} &+ \text{H} &\rightleftharpoons & \text{H}_2 &+ \text{OH}
\end{align*}
\]

So the first and third reactions could be chosen as the independent set of two reactions. For this example, any two of the reactions comprise an independent set.
Consider the stoichiometric matrix for the water gas shift reaction

\[
\nu = \begin{bmatrix}
0 & 1 & 0 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 & 0 & 0 \\
1 & 0 & -1 & 0 & -1 & 1
\end{bmatrix}
\]

Whether or not the \textit{i}th reaction is a linear combination of the other reactions is the same as whether or not the \textit{i}th row of the \(\nu\) matrix is 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 \textbf{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 \(\nu\).
More species than reactions

Our first use of mathematics to tell us something nonobvious about reactions
Show that mass conservation implies that any independent set of reactions has more species than reactions.
We know that mass conservation is equivalent to

$$\nu M = 0$$

Consider the columns of the \( \nu \) matrix as column vectors.
Matrix-vector multiplication can be expressed as a linear combination of the columns of \( \nu \) with the elements of the \( M \) vector as the coefficients in the linear combination

$$\nu M = \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1n_s} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{n_i 1} & \nu_{n_i 2} & \cdots & \nu_{n_i n_s} \end{bmatrix} \begin{bmatrix} M_1 \\ M_2 \\ \vdots \\ M_{n_s} \end{bmatrix}$$

$$= \begin{bmatrix} \nu_{11} \\ \vdots \\ \nu_{n_i 1} \end{bmatrix} M_1 + \begin{bmatrix} \nu_{12} \\ \vdots \\ \nu_{n_i 2} \end{bmatrix} M_2 + \cdots + \begin{bmatrix} \nu_{1n_s} \\ \vdots \\ \nu_{n_i n_s} \end{bmatrix} M_{n_s}$$

$$= \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$
More species than reactions

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

The fine print

Notice that one must consider linearly independent reactions for the statement in the example to be true.

$$
\begin{align*}
2\text{NO} + \text{O}_2 & \rightleftharpoons 2\text{NO}_2 \\
4\text{NO} + 2\text{O}_2 & \rightleftharpoons 4\text{NO}_2 \\
6\text{NO} + 3\text{O}_2 & \rightleftharpoons 6\text{NO}_2 \\
8\text{NO} + 4\text{O}_2 & \rightleftharpoons 8\text{NO}_2
\end{align*}
$$

$$
\nu = \begin{bmatrix}
-2 & -1 & 2 \\
-4 & -2 & 4 \\
-6 & -3 & 6 \\
-8 & -4 & 8
\end{bmatrix}
$$
Maximal sets of linearly independent reactions.

Please read the book for this discussion.
I will skip over this in lecture.

---

**Reaction Rates**

Consider the third reaction in the CVD chemistry

\[ \text{SiH}_4 + \text{SiH}_2 \rightleftharpoons \text{Si}_2\text{H}_6 \]

The **reaction rate**, \( r \), is defined as the number of times this reaction event takes place per time per volume.
Turn SiH₄, SiH₂ and Si₂H₆ molecules loose in a box of some fixed volume V.

The reaction extent, $\varepsilon$, keeps track of the number of times this reaction event occurs. Count up the net number of times an SiH₄ molecule hits an SiH₂ molecule and turned into an Si₂H₆ 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 $\Delta t$.

The reaction rate is then

$$r = \frac{\Delta \varepsilon}{\Delta t V}$$
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 \( \varepsilon \) is positive and the reaction rate is positive.

If the reverse event occurs more often than the forward event, then the change in \( \varepsilon \) and reaction rate are negative.

If the system is at equilibrium, then the change in \( \varepsilon \) is zero and the forward and reverse events occur in equal numbers.

Units of \( r \)

The extent \( \varepsilon \) is a number of molecular change events.
The units of \( r \) are molecules/(time·volume).
Or divide by Avogadro’s number,
The units of extent are moles and the units of reaction rate are moles/(time·volume)
Ignore the discrete nature of the molecules. How? 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.

### Production Rates

It is difficult to measure reaction rates directly, because we do not directly sense molecular transformation events. We can measure concentrations. A major goal is 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.

**production rate**, $R$, the rate at which a given species is produced (moles/(time-volume)) due to the chemical reactions taking place.
Production Rates

\[ \text{SiH}_4 + \text{SiH}_2 \rightleftharpoons \text{Si}_2\text{H}_6 \]

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.

Production Rates

The three production rates are:

\[ R_{\text{SiH}_4} = -r \]
\[ R_{\text{SiH}_2} = -r \]
\[ R_{\text{Si}_2\text{H}_6} = r \]
The production rate vector, \( R \),

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

The connection between the three production rates and the single reaction rate

\[
R = \begin{bmatrix}
-1 \\
-1 \\
1
\end{bmatrix} r
\]

Our friend, the stoichiometric matrix, emerges

\[
\text{SiH}_4 + \text{SiH}_2 \rightleftharpoons \text{Si}_2\text{H}_6
\]

\[
\nu = [-1 \ -1 \ 1]
\]

\[
R = \begin{bmatrix}
-1 \\
-1 \\
1
\end{bmatrix} r
\]

The column vector in this equation is the transpose of the row vector \( \nu \)
Recall the water gas shift

\[
\begin{align*}
H_2O + CO & \rightleftharpoons CO_2 + H_2 \\
H_2O + H & \rightleftharpoons H_2 + OH \\
OH + CO & \rightleftharpoons CO_2 + H
\end{align*}
\]

Three reaction rates are required to track all three reactions. 
\( r_i \) denotes the \( i \)th reaction rate

\[
R_H = (0) \ r_1 + (-1) \ r_2 + (1) \ r_3 = -r_2 + r_3
\]

- Production rate of atomic hydrogen, H
- H is consumed in the second reaction
- H is produced in the third reaction.
Multiple Reactions

\[
\begin{align*}
H_2O + CO & \rightleftharpoons CO_2 + H_2 \\
H_2O + H & \rightleftharpoons H_2 + OH \\
OH + CO & \rightleftharpoons CO_2 + H
\end{align*}
\]

- production rate of molecular hydrogen, \(H_2\).
- \(H_2\) is produced in the first reaction
- \(H_2\) is produced in the second reaction

\[
R_{H_2} = (1) \ r_1 + (1) \ r_2 + (0) \ r_3 = r_1 + r_2
\]

Fill in remaining four species

\[
\begin{bmatrix}
R_H \\
R_{H_2} \\
R_{OH} \\
R_{H_2O} \\
R_{CO} \\
R_{CO_2}
\end{bmatrix} = \begin{bmatrix}
0 & -1 & 1 \\
1 & 1 & 0 \\
0 & 1 & -1 \\
-1 & -1 & 0 \\
-1 & 0 & -1 \\
1 & 0 & 1
\end{bmatrix} \begin{bmatrix}
r_1 \\
r_2 \\
r_3
\end{bmatrix}
\]
\[
\begin{bmatrix}
R_H \\
R_{H_2} \\
R_{OH} \\
R_{H_2O} \\
R_{CO} \\
R_{CO_2}
\end{bmatrix}
= \begin{bmatrix}
0 & -1 & 1 \\
1 & 1 & 0 \\
0 & 1 & -1 \\
-1 & -1 & 0 \\
-1 & 0 & -1 \\
1 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\nu_1 \\
\nu_2 \\
\nu_3
\end{bmatrix}
\begin{bmatrix}
A_1 \\
A_2 \\
A_3 \\
A_4 \\
A_5 \\
A_6
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]

The two matrices are transposes of each other.

\[
R = \nu^T \cdot r
\]

in which \( \nu^T \) denotes the transpose of the stoichiometric matrix.

We 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.
Computing $R$ from $r$ is a simple
Consider again the water gas shift reaction chemistry,

\[
\begin{bmatrix}
0 & 1 & 0 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 & 0 & 0 \\
1 & 0 & -1 & 0 & -1 & 1
\end{bmatrix}
\begin{bmatrix}
H \\
H_2 \\
OH \\
H_2O \\
CO \\
CO_2
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]

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),

Assume we know the reaction rates are:

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

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

\[
\begin{bmatrix}
R_H \\
R_{H_2} \\
R_{OH} \\
R_{H_2O} \\
R_{CO} \\
R_{CO_2}
\end{bmatrix}
= \begin{bmatrix}
0 & -1 & 1 \\
1 & 1 & 0 \\
0 & 1 & -1 \\
-1 & -1 & 0 \\
-1 & 0 & -1 \\
1 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 \\
2 \\
3
\end{bmatrix}
= \begin{bmatrix}
1 \\
3 \\
-1 \\
-3 \\
-4 \\
4
\end{bmatrix}
\]
Computing Production Rates from Reaction Rates

\[
\begin{align*}
\text{H}_2\text{O} + \text{CO} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\text{H}_2\text{O} + \text{H} & \rightleftharpoons \text{H}_2 + \text{OH} \\
\text{OH} + \text{CO} & \rightleftharpoons \text{CO}_2 + \text{H} \\
\end{align*}
\]

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

The effect of the three reactions is to produce H, H\textsubscript{2} and CO\textsubscript{2}, and to consume OH, H\textsubscript{2}O and CO at the given rates.

Computing Reaction Rates from Production Rates

Linearly independent set: the first two water gas shift reactions

\[
\begin{align*}
\text{H}_2\text{O} + \text{CO} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \\
\text{H}_2\text{O} + \text{H} & \rightleftharpoons \text{H}_2 + \text{OH} \\
\end{align*}
\]

Production rates:

\[
\begin{bmatrix}
    R_\text{H} \\
    R_{\text{H}_2} \\
    R_{\text{OH}} \\
    R_{\text{H}_2\text{O}} \\
    R_{\text{CO}} \\
    R_{\text{CO}_2} \\
\end{bmatrix} =
\begin{bmatrix}
    0 & -1 \\
    1 & 1 \\
    0 & 1 \\
    -1 & -1 \\
    -1 & 0 \\
    1 & 0 \\
\end{bmatrix}
\begin{bmatrix}
    r_1 \\
    r_2 \\
\end{bmatrix}
\]
We can compute the production rates when the two reaction rates are
\[
\begin{bmatrix}
  r_1 \\
  r_2
\end{bmatrix}
= \begin{bmatrix}
  1 \\
  2
\end{bmatrix}
\]
we obtain
\[
R = \begin{bmatrix}
  -2 \\
  3 \\
  2 \\
  -3 \\
  -1 \\
  1
\end{bmatrix}
\]
Assume the production rate of H is in error
\[
R_{meas} = \begin{bmatrix}
  -2.1 \\
  3 \\
  2 \\
  -3 \\
  -1 \\
  1
\end{bmatrix}
\]
Six equations and only two unknowns, the equations are inconsistent, no exact solution.
Least-Squares Approach:
Square the error in each equation and sum
Inconsistent equations (no exact solution).

\[ R = \nu^T r \]

Least-squares solution.

\[ r = (\nu \nu^T)^{-1}\nu R \]

Impact of measurement error

\[
R_{\text{meas}} = \begin{bmatrix}
-2.1 \\
3 \\
2 \\
-3 \\
-1 \\
1
\end{bmatrix}
\Rightarrow r_{\text{est}} = \begin{bmatrix}
0.98333 \\
2.03333
\end{bmatrix}
\]

instead of the correct

\[
r = \begin{bmatrix}
1 \\
2
\end{bmatrix}
\]

A small error in the H production rate has translated into small errors in both inferred reaction rates.
Impact of measurement error

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

Take each column of $R_{\text{meas}}$, and compute the least squares estimate of $r$ for that measurement

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

Estimating reaction rates from production rates

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.

Summary — stoichiometric matrix

Keeping track of the stoichiometry of chemical reactions,

\[ \sum_{j=1}^{n_s} \nu_{ij} A_j = 0, \quad i = 1, 2, \ldots, n_r \]

\( A_j \) represents chemical species \( j, j = 1, \ldots, n_s \) \( n_s \) species in the reaction network \( \nu_{ij} \) is the stoichiometric coefficient for species \( j \) in reaction \( i, i = 1, \ldots, n_r \) \( n_r \) reactions in the network

\[ \nu A = 0 \]
• 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.
• The rank of a matrix is the number of linearly independent rows (equivalently columns) of the matrix.
• The rank of $\nu$ is the number of linearly independent reactions in the network.

Summary — Reaction and Production Rates

• 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,

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

$$ R = \nu^T r $$
Given the rates of reactions, it is a simple matter to compute the species production rates. In general, one cannot solve uniquely the reverse problem, namely given observed production rates, compute the corresponding reaction rates. We require 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.

\[ R = \nu^T r \]  

(2.60)

If the observed production rates contain experimental errors, there may not exist an exact solution of reaction rates, \( r \), that satisfy Equation 2.60. Find 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

\( A_j \) \( j \)th species in the reaction network
\( a_{jl} \) chemical formula number in species \( j \) corresponding to element \( l \)
\( E^l \) \( l \)th 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 \( j \)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
\( \nu_{ij} \) stoichiometric number for the \( j \)th species in the \( i \)th reaction

References I

M. E. Coltrin, R. J. Kee, and J. A. Miller.
A mathematical model of the coupled fluid mechanics and chemical kinetics in a chemical vapor deposition reactor.