

# CHAPTER 2: The Stoichiometry of Reactions—Introduction

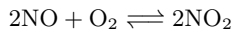
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- Stoichiometry: the determination of the proportions in which chemical elements combine or are produced and the weight relations in any chemical reaction.<sup>1</sup>
- the stoichiometric matrix,  $\nu$
- linearly independent reactions
- mass conservation in chemical reactions
- reaction rates,  $r_i$ ,  $i = 1, \dots, n_r$
- production rates,  $R_j$ ,  $j = 1, \dots, n_s$

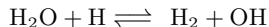
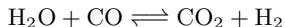
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<sup>1</sup>Webster's New World College Dictionary, fourth edition, 2000.

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



One chemical reaction and three different chemical species:  
NO, O<sub>2</sub>, and NO<sub>2</sub>.

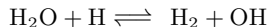
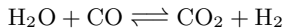


Three chemical reactions and six different chemical species:

H, H<sub>2</sub>, OH, H<sub>2</sub>O, CO, and CO<sub>2</sub>.

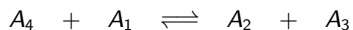
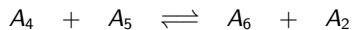
Let  $A_j$  represent the  $j$ th species

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



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





$$-A_4 - A_5 + A_6 + A_2 = 0$$

$$-A_4 - A_1 + A_2 + A_3 = 0$$

$$-A_3 - A_5 + A_6 + A_1 = 0$$

**products** have **positive** coefficients  
**reactants** have **negative** coefficients

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

**stoichiometric matrix  $\nu$**

**A** column vector of  $A_j$ ,  $j = 1, \dots, 6$

$$\boxed{\nu \mathbf{A} = \mathbf{0}}$$

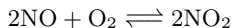
$$\nu \mathbf{A} = \mathbf{0}$$

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

$i$  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

## Stoichiometric matrix for a single reaction

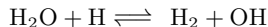


$A_1 = \text{NO}$ ,  $A_2 = \text{O}_2$ ,  $A_3 = \text{NO}_2$ .

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

The stoichiometric matrix for a single reaction is a row vector.

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



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

Instead of  $A_1 = \text{H}$  and  $A_6 = \text{CO}_2$ , what is the stoichiometric matrix if  $A_1$  is  $\text{CO}_2$  and  $A_6$  is  $\text{H}$ ?

Modified species 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  $A'_6 = \text{H}$ .

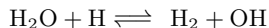
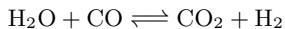
$$A'_4 + A'_5 \iff A'_1 + A'_2$$

$$A'_4 + A'_6 \iff A'_2 + A'_3$$

$$A'_3 + A'_5 \iff A'_1 + A'_6$$

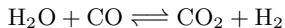
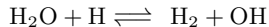
$$\nu' = \begin{array}{c} \downarrow \qquad \qquad \qquad \downarrow \\ \begin{bmatrix} 1 & 1 & 0 & -1 & -1 & 0 \\ 0 & 1 & 1 & -1 & 0 & -1 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \end{array}$$

- 1 Switching species one and six in the **A** implies switching the first and sixth **columns** in the stoichiometric matrix.
- 2 Connection of the **columns** of  $\nu$  and the **species** taking part in the reactions.
- 3 The  $j$ th column of the  $\nu$  matrix supplies the stoichiometric numbers of the  $j$ th species in all of the reactions.



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

Exchange the first and third reactions



$$A_3 + A_5 \iff A_6 + A_1$$

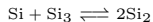
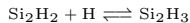
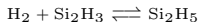
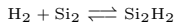
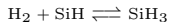
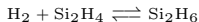
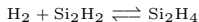
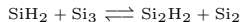
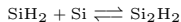
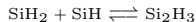
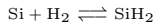
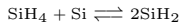
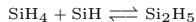
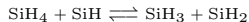
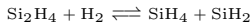
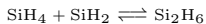
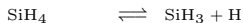
$$A_4 + A_1 \iff A_2 + A_3$$

$$A_4 + A_5 \iff A_6 + A_2$$

$$\nu'' = \begin{array}{l} \longrightarrow \\ \longrightarrow \end{array} \begin{bmatrix} 1 & 0 & -1 & 0 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & -1 & 1 \end{bmatrix}$$

- 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)



- 1 The CVD reactions are a simplified version of 120 reactions that were originally postulated for this reaction network [1].
- 2 Combustion chemistry: several hundred reactions.
- 3 Polymerizations and long-chain-producing reactions: thousands of species and associated reactions.
- 4 The stoichiometry of these complex problems is intractable if we do not develop a systematic, automated procedure.

There are 20 reactions,  $n_r = 20$ .

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>.

$$\nu = \begin{bmatrix} 0 & 1 & 0 & 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & -1 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$\nu$  is a  $20 \times 14$  matrix; it contains many zero entries.

A matrix with many zero entries is called sparse

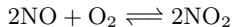
Physical fact: very few molecules can take part in a particular reaction. Why?

All of the reactions in the CVD chemistry are unimolecular or bimolecular.

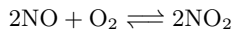
Show conservation of mass in a chemical reaction can be stated as

$$\nu M = 0$$

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



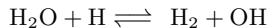
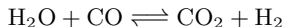
- In a chemical reaction, the number of molecules is *not* conserved
- In a chemical (i.e. not nuclear) reaction, elements *are* conserved
- In a chemical (i.e. not nuclear) reaction, mass *is* conserved



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

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

$$\nu \mathbf{M} = 0$$



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

$$\mathbf{M} = [ M_{\text{H}} \quad M_{\text{H}_2} \quad M_{\text{OH}} \quad M_{\text{H}_2\text{O}} \quad M_{\text{CO}} \quad M_{\text{CO}_2} ]^T$$

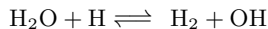
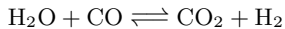
the superscript  $T$  means the transpose of the matrix

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

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

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

$$\nu M = 0$$



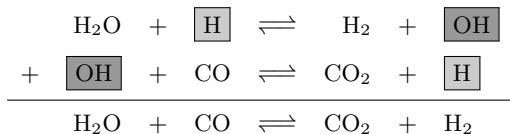
Question: can we express any reaction in the network as a linear combination of the other reactions?

If we can, then the set of reactions is not independent.

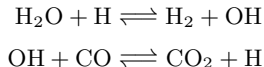
Can we express the first reaction as a linear combination of the second and third reactions?

# Independent Reactions

By inspection, the first reaction is the sum of the second and third reactions, so the set of three reactions is not independent.

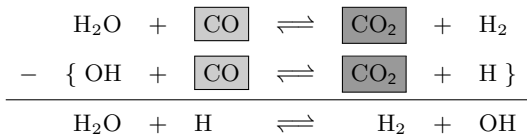


If we deleted the first reaction from the network, would the remaining two reactions be independent? Why or why not?



There is nothing *wrong* with the first reaction

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



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  $i$ th **reaction** is a linear combination of the other reactions is the same as whether or not the  $i$ 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 **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  $\nu$ .

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

$$\nu \mathbf{M} = \mathbf{0}$$

Consider the columns of the  $\nu$  matrix as column vectors.

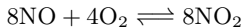
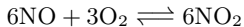
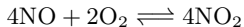
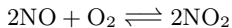
Matrix-vector multiplication can be expressed as a linear combination of the columns of  $\nu$  with the elements of the  $\mathbf{M}$  vector as the coefficients in the linear combination

$$\begin{aligned}
 \nu \mathbf{M} &= \begin{bmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1n_s} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{n_i 1} & \nu_{n_i 2} & \cdots & \nu_{n_i n_s} \end{bmatrix} \begin{bmatrix} M_1 \\ M_2 \\ \vdots \\ M_{n_s} \end{bmatrix} \\
 &= \begin{bmatrix} \nu_{11} \\ \vdots \\ \nu_{n_i 1} \end{bmatrix} M_1 + \begin{bmatrix} \nu_{12} \\ \vdots \\ \nu_{n_i 2} \end{bmatrix} M_2 + \cdots + \begin{bmatrix} \nu_{1n_s} \\ \vdots \\ \nu_{n_i n_s} \end{bmatrix} M_{n_s} \\
 &= \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}
 \end{aligned}$$

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),  $n_s > n_r$  and  $\nu$  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.

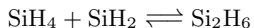


$$\nu = \begin{bmatrix} -2 & -1 & 2 \\ -4 & -2 & 4 \\ -6 & -3 & 6 \\ -8 & -4 & 8 \end{bmatrix}$$

## Maximal sets of linearly independent reactions.

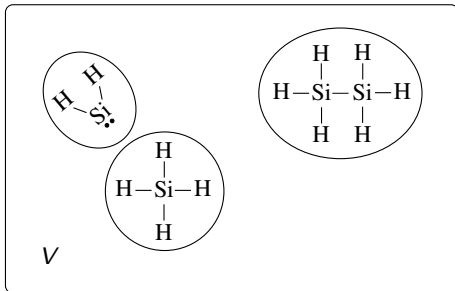
Please read the book for this discussion.  
I will skip over this in lecture.

Consider the third reaction in the CVD chemistry



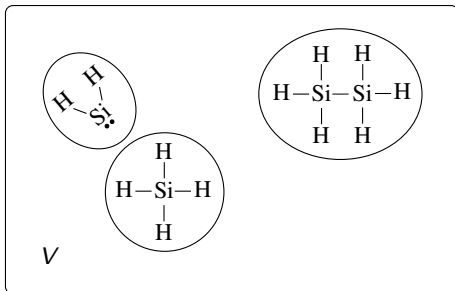
The **reaction rate**,  $r$ , is defined as the number of times this reaction event takes place per time per volume.

# Reaction rate for $\text{SiH}_2 + \text{SiH}_4 \rightleftharpoons \text{Si}_2\text{H}_6$



Turn  $\text{SiH}_4$ ,  $\text{SiH}_2$  and  $\text{Si}_2\text{H}_6$  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  $\text{SiH}_4$  molecule hits an  $\text{SiH}_2$  molecule and turned into an  $\text{Si}_2\text{H}_6$  molecule during a short period of time.

# Reaction rate for $\text{SiH}_2 + \text{SiH}_4 \rightleftharpoons \text{Si}_2\text{H}_6$



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

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

## Sign of $r$ , forward or reverse?

- 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.

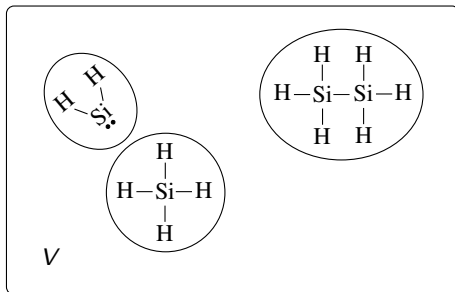
The extent  $\varepsilon$  is a number of molecular change events.

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)

## Continuum assumption



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.

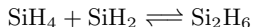
It is difficult to measure reaction rates directly, because we do not directly sense molecular transformation events.

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.



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.

The three production rates are:

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

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

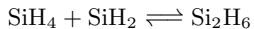
$$R_{\text{Si}_2\text{H}_6} = r$$

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

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

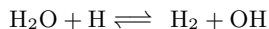


$$\boldsymbol{\nu} = [-1 \quad -1 \quad 1]$$

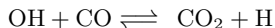
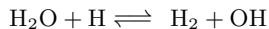
$$\mathbf{R} = \begin{bmatrix} -1 \\ -1 \\ 1 \end{bmatrix} r$$

The column vector in this equation is the transpose of the row vector  $\boldsymbol{\nu}$

Recall the water gas shift

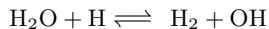
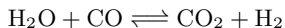


Three reaction rates are required to track all three reactions.  
 $r_i$  denotes the  $i$ th reaction rate



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

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



- production rate of molecular hydrogen,  $\text{H}_2$ .
- $\text{H}_2$  is produced in the first reaction
- $\text{H}_2$  is produced in the second reaction

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

Fill in remaining four species

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

$$\begin{bmatrix} R_H \\ R_{H_2} \\ R_{OH} \\ R_{H_2O} \\ R_{CO} \\ R_{CO_2} \end{bmatrix} = \begin{bmatrix} 0 & -1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \\ -1 & -1 & 0 \\ -1 & 0 & -1 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} \quad \begin{bmatrix} 0 & 1 & 0 & -1 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \end{bmatrix} = \begin{bmatrix} C \\ C \\ C \\ C \\ C \\ C \end{bmatrix}$$

The two matrices are transposes of each other.

$$R = \nu^T r$$

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,

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

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:

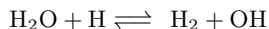
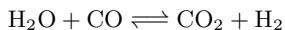
$$\begin{bmatrix} R_{\text{H}} \\ R_{\text{H}_2} \\ R_{\text{OH}} \\ R_{\text{H}_2\text{O}} \\ R_{\text{CO}} \\ R_{\text{CO}_2} \end{bmatrix} = \begin{bmatrix} 0 & -1 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & -1 \\ -1 & -1 & 0 \\ -1 & 0 & -1 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix}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



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

The effect of the three reactions is to produce H, H<sub>2</sub> and CO<sub>2</sub>, and to consume OH, H<sub>2</sub>O and CO at the given rates.

Linearly independent set: the first two water gas shift reactions



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

$$\mathbf{R} = \begin{bmatrix} -2 \\ 3 \\ 2 \\ -3 \\ -1 \\ 1 \end{bmatrix}$$

Assume the production rate of H is in error

$$R_{\text{meas}} = \begin{bmatrix} -2.1 \\ 3 \\ 2 \\ -3 \\ -1 \\ 1 \end{bmatrix}$$

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.

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

$$\mathbf{R}_{\text{meas}} = \begin{bmatrix} -2.1 \\ 3 \\ 2 \\ -3 \\ -1 \\ 1 \end{bmatrix} \Rightarrow \mathbf{r}_{\text{est}} = \begin{bmatrix} 0.98333 \\ 2.03333 \end{bmatrix}$$

instead of the *correct*

$$\mathbf{r} = \begin{bmatrix} 1 \\ 2 \end{bmatrix}$$

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

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

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

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

## Estimating reaction rates from production rates

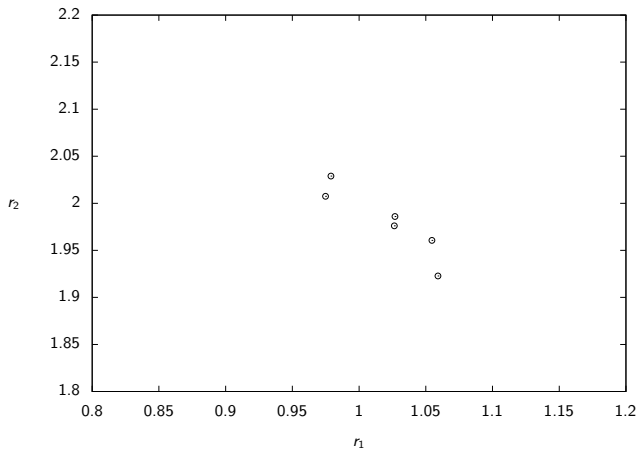
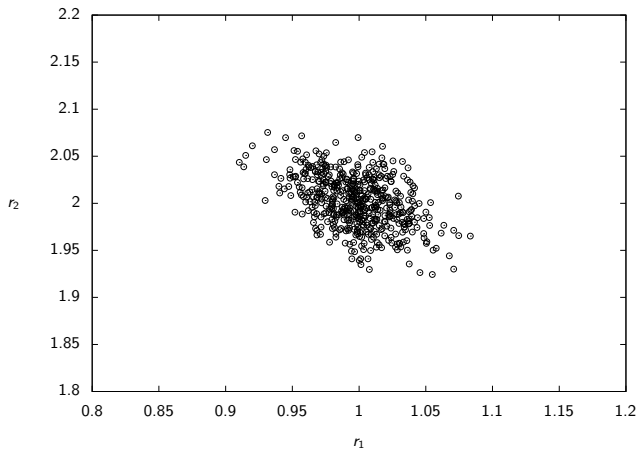


Figure 2.2: Estimated reaction rates from six production rate measurements subject to measurement noise.

## Estimating reaction rates from production rates



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

Keeping track of the stoichiometry of chemical reactions,

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

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

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

- 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.
- 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

- 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,

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

$$\mathbf{R} = \boldsymbol{\nu}^T \mathbf{r}$$

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.

$$R = \nu^T r \quad (2.60)$$

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.

$A_j$	$j$ 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, $i = 1, 2, \dots, n_r$
$j$	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
$\nu_{ij}$	stoichiometric number for the $j$ th species in the $i$ th reaction



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.  
*J. Electrochem. Soc.*, 131(2):425–434, 1984.