

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.¹
- the stoichiometric matrix, ν
- linearly independent reactions
- mass conservation in chemical reactions
- reaction rates, r_i , $i = 1, \dots, n_r$

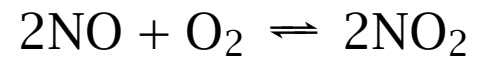
¹Webster's New World College Dictionary, fourth edition, 2000.

- production rates, R_j , $j = 1, \dots, n_s$

Chemical Reactions and Stoichiometry

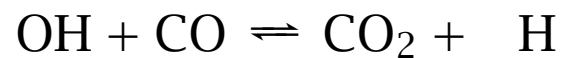
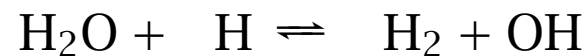
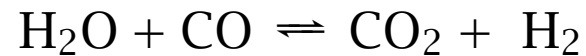
1. Nitric oxide, smog formation in the atmosphere. 1 reaction among 3 species.
2. Water-gas shift reaction. 3 reactions among 6 species.
3. Chemical vapor deposition. 20 reactions among 14 species.

Nitric Oxide



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

Water-Gas Shift Reaction

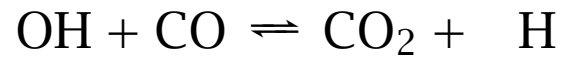
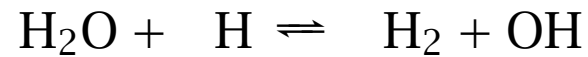
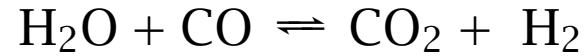


Three chemical reactions and six different chemical species:
H, H₂, OH, H₂O, CO, and CO₂.

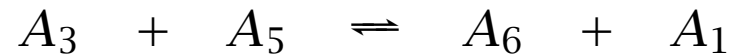
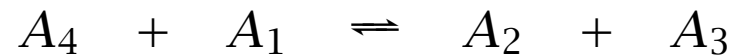
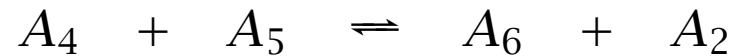
Let A_j represent the j th species

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

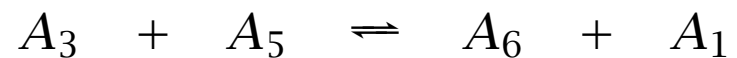
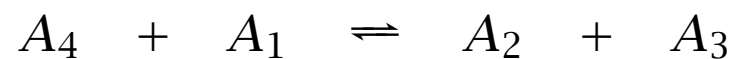
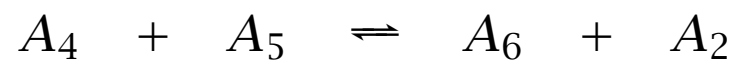
Species Vector and Sign Convention



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



Species Vector and Sign Convention



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

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

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

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

The Stoichiometric Matrix

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

stoichiometric matrix ν

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

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

The i th reaction and the j th species

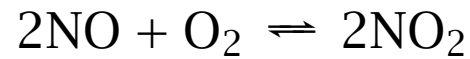
$$\mathbf{vA} = \mathbf{0}$$

$$\sum_{j=1}^{n_s} \mathbf{v}_{ij} A_j = 0, \quad i = 1, \dots, n_r \quad (1)$$

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



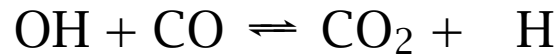
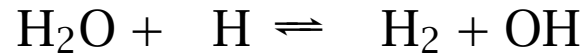
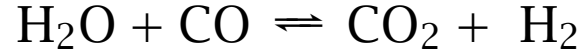
$A_1 = \text{NO}$, $A_2 = \text{O}_2$, $A_3 = \text{NO}_2$.

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

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

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

Columns of ν



$A_1 = \text{H}$, $A_2 = \text{H}_2$, $A_3 = \text{OH}$, $A_4 = \text{H}_2\text{O}$, $A_5 = \text{CO}$, 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 CO_2 and A_6 is 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 $A'_6 = \text{H}$.

Columns of \mathbf{v}

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

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

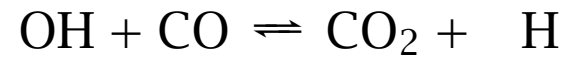
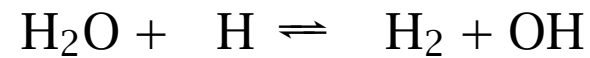
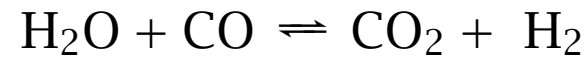
$$A'_3 + A'_5 \Rightarrow A'_1 + A'_6$$

$$\mathbf{v}' = \begin{array}{c} \downarrow \qquad \qquad \qquad \downarrow \\ \left[\begin{array}{cccccc} 1 & 1 & 0 & -1 & -1 & 0 \\ 0 & 1 & 1 & -1 & 0 & -1 \\ 1 & 0 & -1 & 0 & -1 & 1 \end{array} \right] \end{array}$$

Columns of ν

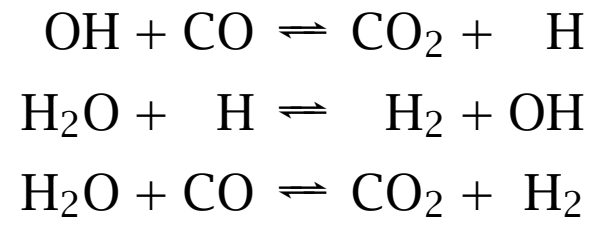
1. Switching species one and six in the A implies switching the first and sixth **columns** in the stoichiometric matrix.
2. Connection of the **columns** of ν and the **species** taking part in the reactions.
3. The j th column of the ν matrix supplies the stoichiometric numbers of the j th species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

Rows of ν



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

Exchange the first and third reactions



Rows of ν

$$A_3 + A_5 \rightleftharpoons A_6 + A_1$$

$$A_4 + A_1 \rightleftharpoons A_2 + A_3$$

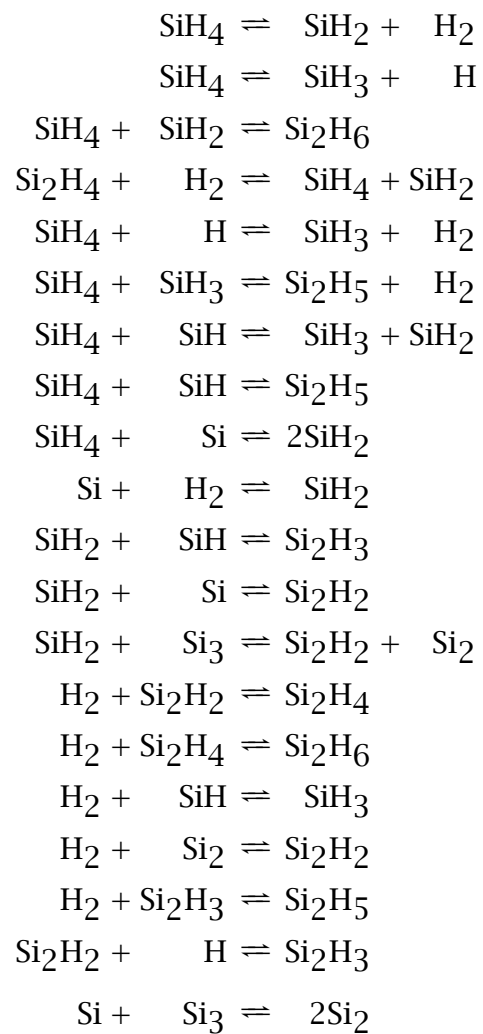
$$A_4 + A_5 \rightleftharpoons A_6 + A_2$$

$$\nu'' = \begin{array}{l} \rightarrow \\ \rightarrow \end{array} \left[\begin{array}{cccccc} 1 & 0 & -1 & 0 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & -1 & 1 \end{array} \right]$$

Rows of ν

- Exchanging the orders of the first and third reactions causes us to exchange the first and third **rows** in the ν matrix
- Connection of the **rows** of ν 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)



(2)

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.

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, H₂, Si, SiH, SiH₂, SiH₃, SiH₄, Si₂, Si₂H₂, Si₂H₃, Si₂H₄, Si₂H₅, Si₂H₆, Si₃.

Stoichiometric matrix for CVD chemistry

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

Stoichiometric matrix for CVD chemistry

ν is a 20×14 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.

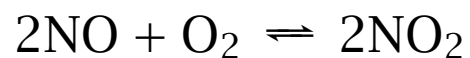
Conservation of mass

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

$$\nu M = 0$$

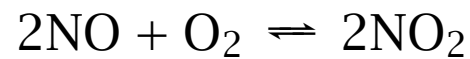
in which M_j is the molecular weight of species j .

What is conserved?



- 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

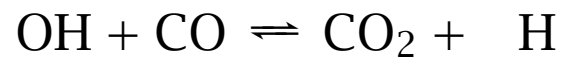
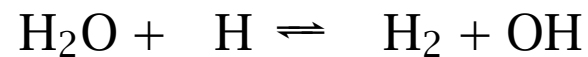
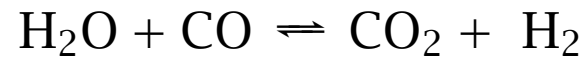


The molecular weights of reactants and products are related by $2M_{\text{NO}} + M_{\text{O}_2} = 2M_{\text{NO}_2}$.

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

$$\mathbf{vM} = 0$$

Conservation of Mass



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

$$\mathbf{M} = \left[\begin{array}{cccccc} M_{\text{H}} & M_{\text{H}_2} & M_{\text{OH}} & M_{\text{H}_2\text{O}} & M_{\text{CO}} & M_{\text{CO}_2} \end{array} \right]^T$$

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

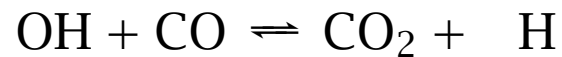
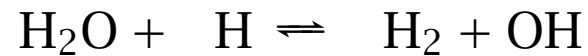
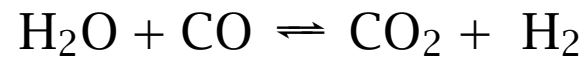
$$M_{\text{CO}_2} + M_{\text{H}_2} - M_{\text{H}_2\text{O}} - M_{\text{CO}} = 0$$

Conservation of Mass

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

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

Independent Reactions



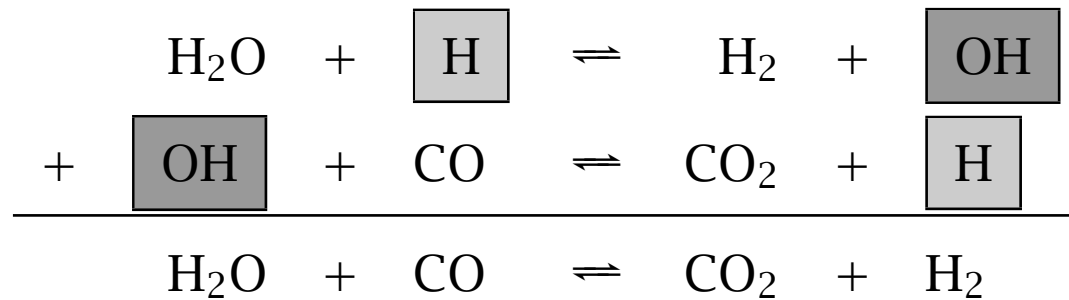
Question: can we express any reaction in the network as a linear combination of the other reactions?

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?

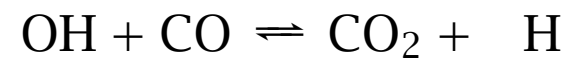
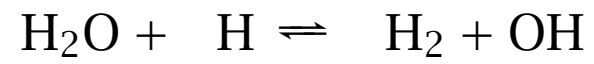
Independent Reactions

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

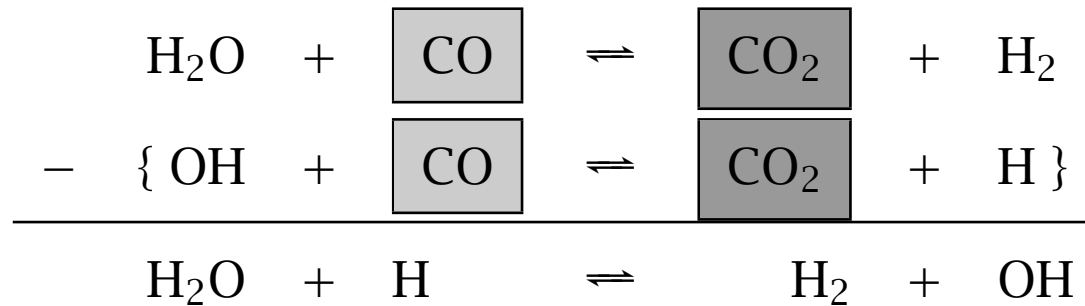
reactions be independent? Why or why not?



Independent Reactions

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.

Independent Reactions

Consider the stoichiometric matrix for the water gas shift reaction

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

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 \mathbf{v} matrix is a linear combination of the other rows.

Independent Reactions

- 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 ν .

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

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

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

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

More species than reactions

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

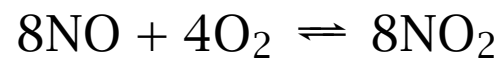
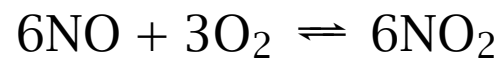
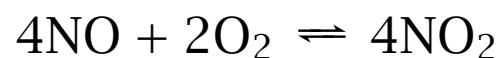
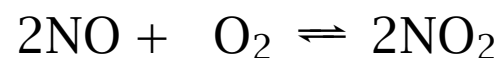
More species than reactions

The last equation implies the columns of $\boldsymbol{\nu}$ 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 $\boldsymbol{\nu}$ 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.



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

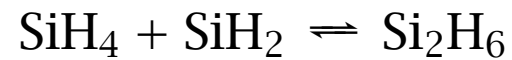
Maximal sets of linearly independent reactions.

Please read the book for this discussion.

I will skip over this in lecture.

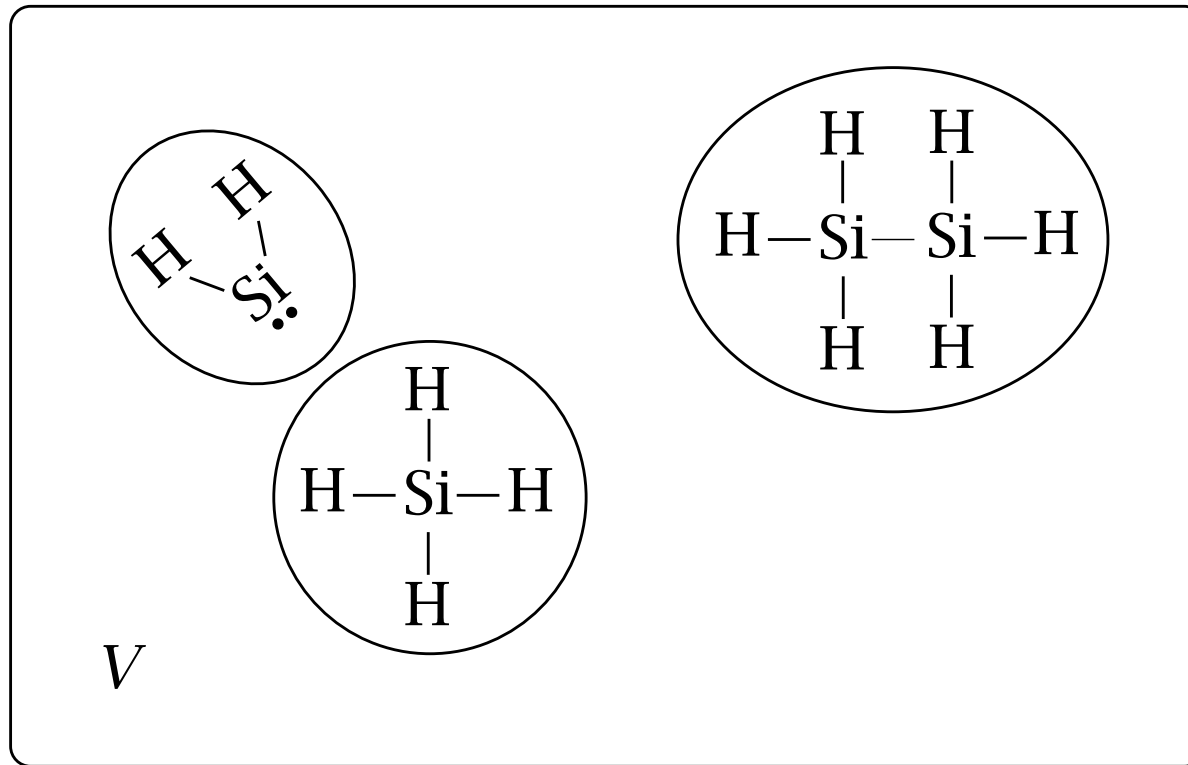
Reaction Rates

Consider the third reaction in the CVD chemistry



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

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



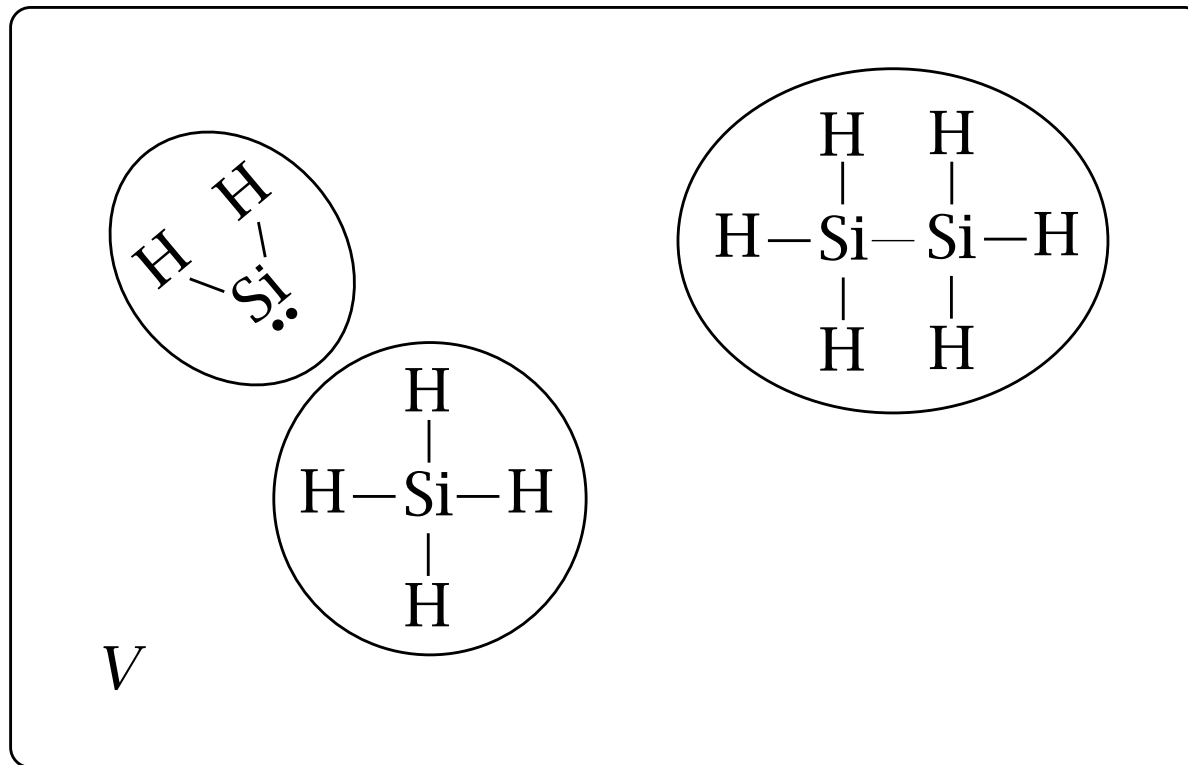
Turn SiH_4 , SiH_2 and Si_2H_6 molecules loose in a box of some fixed volume V

The **reaction extent**, ε , keeps track of the number of times this reaction

event occurs.

Count up the net number of times an SiH_4 molecule hits an SiH_2 molecule and turned into an Si_2H_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 Δt .

The reaction rate is then

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

Sign of r , forward or reverse?

- 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.

Units of r

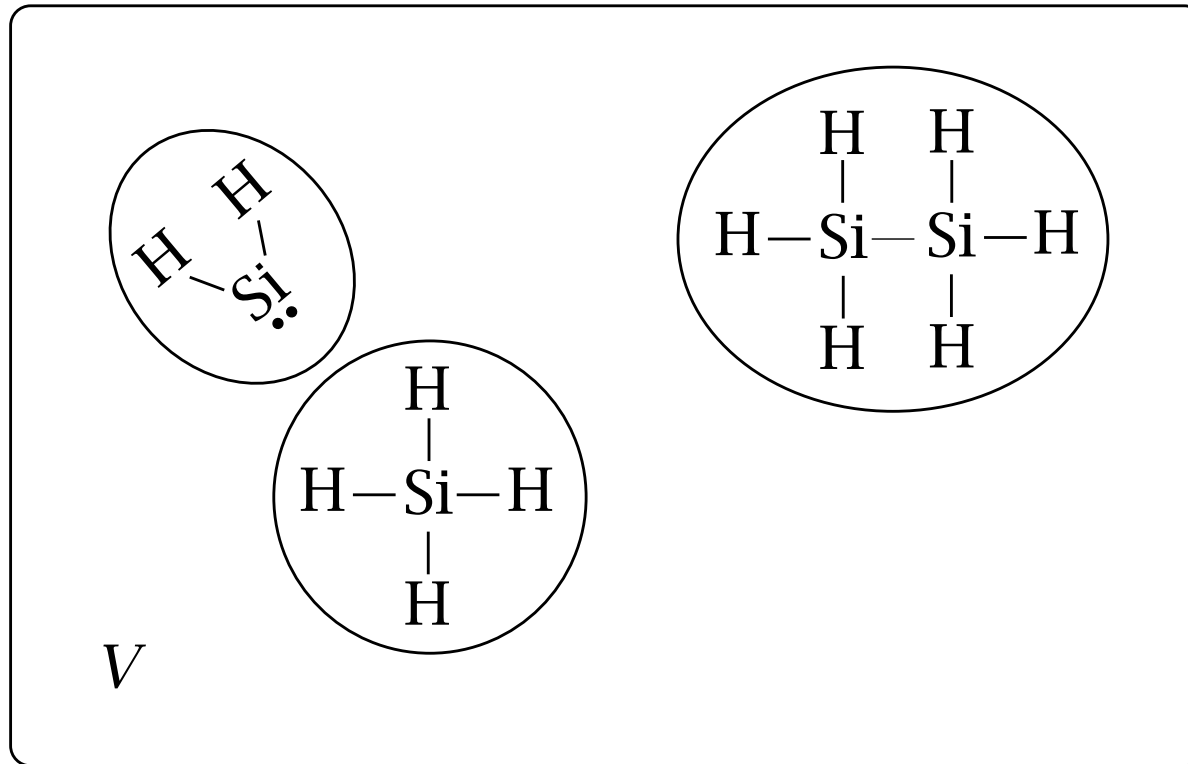
The extent ε is a number of molecular change events.

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.

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



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 , $R_{\text{Si}_2\text{H}_6}$, 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 Si_2H_6 is being produced.

Production Rates

The three production rates are:

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

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

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

Production rate vector

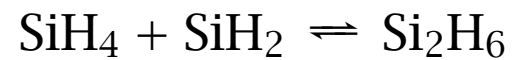
The production rate vector, \mathbf{R} ,

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

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

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

Our friend, the stoichiometric matrix, emerges



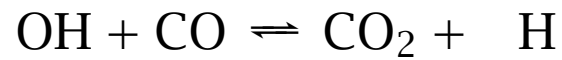
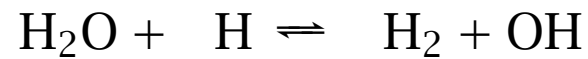
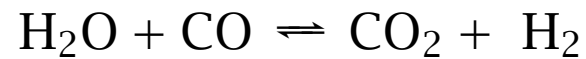
$$\boldsymbol{\nu} = [-1 \quad -1 \quad 1]$$

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

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

Multiple Reactions

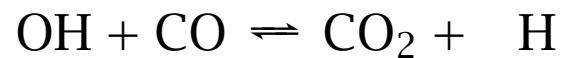
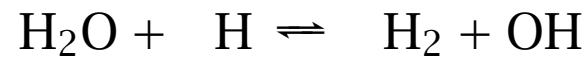
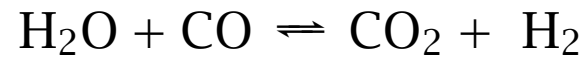
Recall the water gas shift



Three reaction rates are required to track all three reactions.

r_i denotes the i th reaction rate

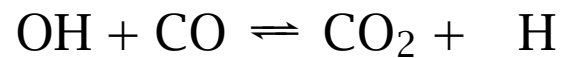
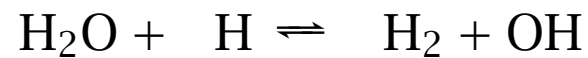
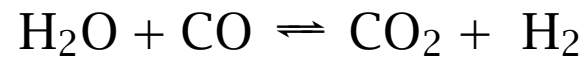
Multiple Reactions



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

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

Multiple Reactions



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

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

Multiple Reactions

Fill in remaining four species

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

Fundamental Relationship

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

The two matrices are transposes of each other.

Fundamental Relationship

$$R = \mathbf{v}^T \mathbf{r}$$

in which \mathbf{v}^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 Production Rates from Reaction Rates

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),

Computing Production Rates from Reaction Rates

Assume we know the reaction rates are:

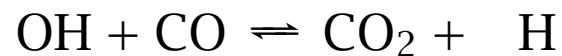
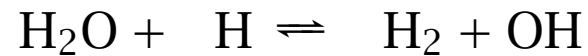
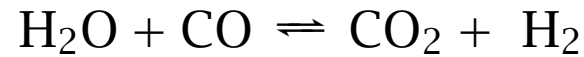
$$\begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$$

The production rates of the six species due to these reactions are then com-

puted 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

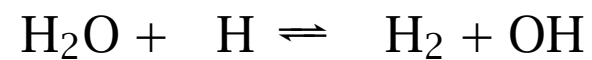
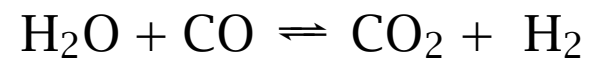


$$\begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$$

The effect of the three reactions is to produce H, H₂ and CO₂, and to consume OH, H₂O and CO at the given rates.

Computing Reaction Rates from Production Rates

Linearly independent set: the first two water gas shift reactions



Production rates:

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

Errors in the Data and Least-Squares Estimation of Rates

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

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

Errors in the Data and Least-Squares Estimation of Rates

Assume the production rate of H is in error

$$\mathbf{R}_{\text{meas}} = \begin{bmatrix} -2.1 \\ 3 \\ 2 \\ -3 \\ -1 \\ 1 \end{bmatrix}$$

Six equations and only two unknowns, the equations are inconsistent, no exact solution.

Errors in the Data and Least-Squares Estimation of Rates

Least-Squares Approach:

Square the error in each equation and sum

Inconsistent equations (no exact solution).

$$R = \mathbf{v}^T \mathbf{r}$$

Least-squares solution.

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

Impact of measurement error

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

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.

Impact of measurement error

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

Take each column of \mathbf{R}_{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

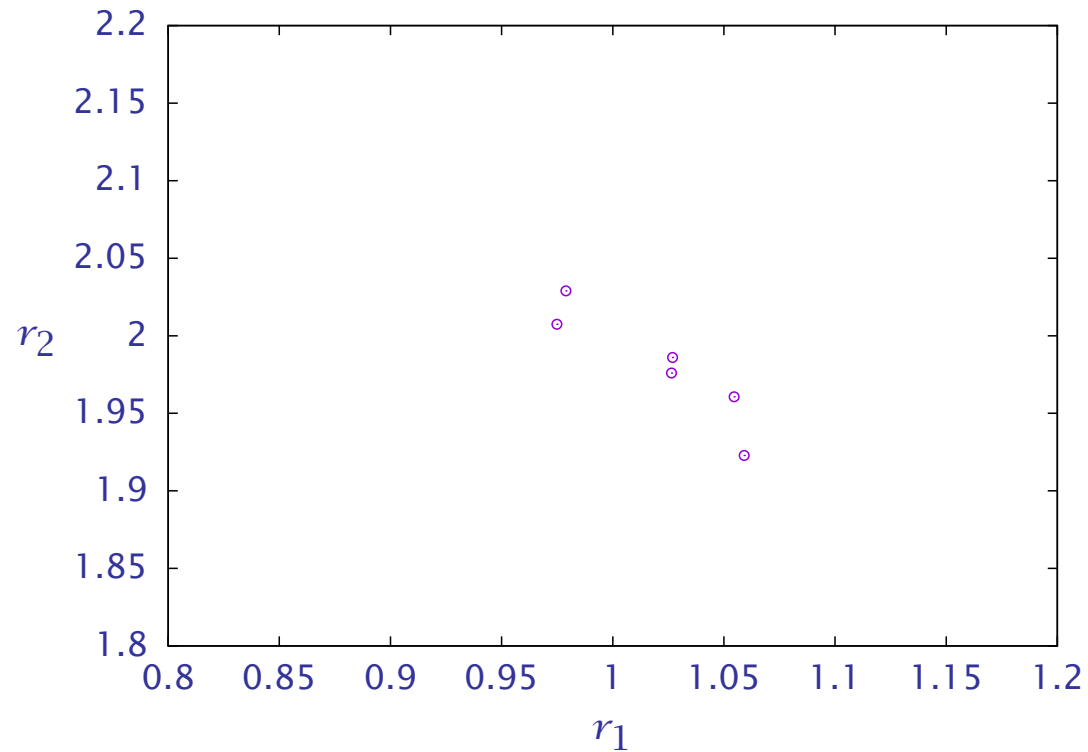


Figure 1: Estimated reaction rates from six production rate measurements subject to measurement noise.

Estimating reaction rates from production rates

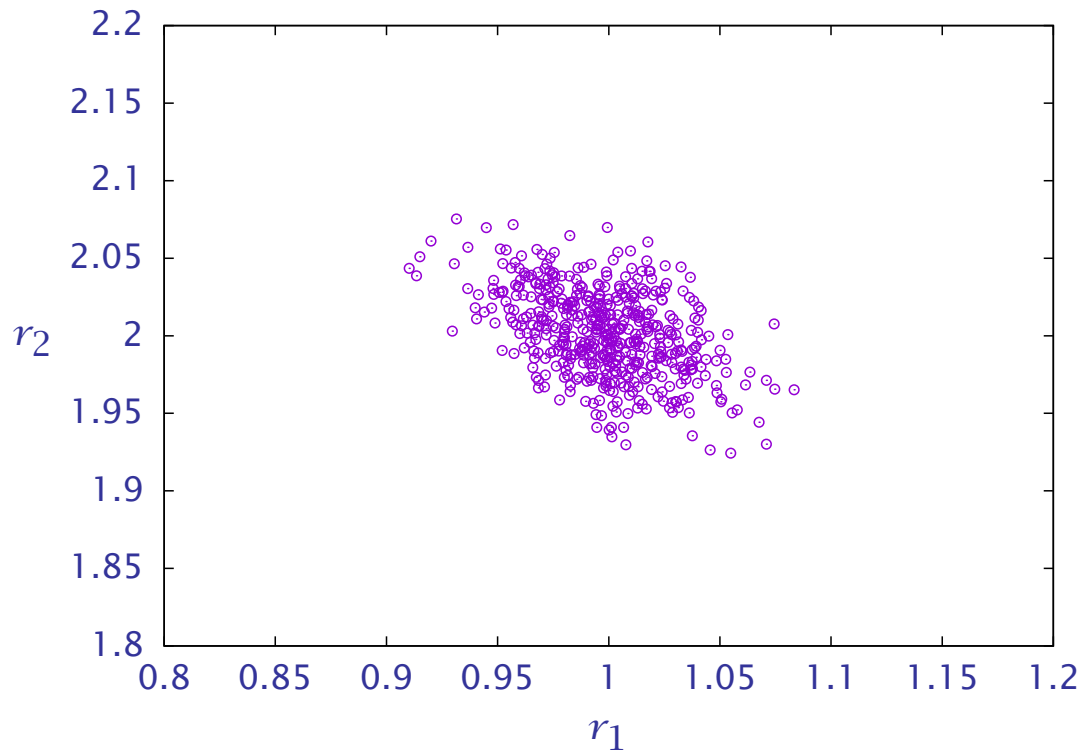


Figure 2: Estimated reaction rates from 500 production rate measurements subject to measurement noise.

Summary — stoichiometric matrix

Keeping track of the stoichiometry of chemical reactions,

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

A_j represents chemical species j , $j = 1, \dots, n_s$ n_s species in the reaction network

ν_{ij} is the stoichiometric coefficient for species j in reaction i , $i = 1, \dots, n_r$ n_r reactions in the network

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

Summary — linear independence

- 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 ν 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,

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

$$\mathbf{R} = \mathbf{v}^T \mathbf{r}$$

Summary — exchanging rates

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.

Summary — measurement and least squares

$$\mathbf{R} = \mathbf{v}^T \mathbf{r} \quad (3)$$

If the observed production rates contain experimental errors, there may not exist an exact solution of reaction rates, \mathbf{r} , that satisfy Equation 3.

Find the reaction rates that *most closely* satisfy Equation 3.

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

References

- [1] 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.