Conversation 28: The Rank of a Stoichiometric Matrix

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MATH3200: Applied Linear Algebra

How about an engineering application of the rank?

Frank: This "rank" is all very abstract. I bet it is useless for real engineering applications!

Theo: Here is a real application. Consider again the system of chemical reactions that we talked about earlier:

1. $A + 2B \rightleftarrows 2C$
2. $A + 2C \rightleftarrows 2D$
3. $A + B \rightleftarrows D$
4. $B + D \rightleftarrows 2C$

Chemists may know that these reactions could *in principle* occur, but may want to know which of them, or at least how many of them *actually occur* in a given context.

Cindy: Didn't you already tell us they do this by observing a vector of net changes over some time interval?

Theo: Yes indeed. And then they would like to extract as much information about the reactions as possible from this vector.

Review: Reaction vectors and net change

Bob: So suppose we observe a net change $\vec{\mathbf{w}} = \begin{bmatrix} -3 \\ -4 \\ 2 \\ 2 \end{bmatrix}$

What can we tell then?

Frank: Is that possible at all?

Bob: We explored a similar question in Module 45.
We can observe $\vec{\mathbf{w}}$ as long as it is a linear combination of the reaction vectors:

$$\vec{\mathbf{v}}_1 = \begin{bmatrix} -1 \\ -2 \\ 2 \\ 0 \end{bmatrix} \qquad \vec{\mathbf{v}}_2 = \begin{bmatrix} -1 \\ 0 \\ -2 \\ 2 \end{bmatrix} \qquad \vec{\mathbf{v}}_3 = \begin{bmatrix} -1 \\ -1 \\ 0 \\ 1 \end{bmatrix} \qquad \vec{\mathbf{v}}_4 = \begin{bmatrix} 0 \\ -1 \\ 2 \\ -1 \end{bmatrix}$$

Question C28.1: Is Bob's $\vec{\mathbf{w}}$ a linear combination of $\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4$?

What does the vector of net changes tell us?

Bob: I chose my $\vec{\mathbf{w}}$ in such a way that

$$\vec{\mathbf{w}} = \begin{bmatrix} -3 \\ -4 \\ 2 \\ 2 \end{bmatrix} = \begin{bmatrix} -1 \\ -2 \\ 2 \\ 0 \end{bmatrix} + \begin{bmatrix} -1 \\ 0 \\ -2 \\ 2 \end{bmatrix} + \begin{bmatrix} -1 \\ -1 \\ 0 \\ 1 \end{bmatrix} + \begin{bmatrix} 0 \\ -1 \\ 2 \\ -1 \end{bmatrix} = \vec{\mathbf{v}}_1 + \vec{\mathbf{v}}_2 + \vec{\mathbf{v}}_3 + \vec{\mathbf{v}}_4$$

So $\vec{\mathbf{w}}$ is a linear combination of the reaction vectors, in symbols:

$\vec{\mathbf{w}} = k_1\vec{\mathbf{v}}_1 + k_2\vec{\mathbf{v}}_2 + k_3\vec{\mathbf{v}}_3 + k_4\vec{\mathbf{v}}_4$ for some coefficients k_1, k_2, k_3, k_4 that represent the net reaction rates.

It follows that my $\vec{\mathbf{w}}$ could be observed as a vector of net changes.

Cindy: The coefficients k_1, k_2, k_3, k_4 represent net reaction rates as I recall, right?

Bob: Right!

Denny: Since your k_1, k_2, k_3, k_4 are all equal to 1 and none of them is zero, we can conclude that every reaction must have occurred!

Question C28.2: What do you think of Denny's observation?

Review: The stoichiometric matrix

Bob: I would agree with you, Denny, *if we actually knew* that these coefficients are all 1. But I am wondering whether we could *deduce* this from the observed vector of net changes alone.

Theo: Let's take a step back and look at the stoichiometric matrix

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

The reaction vectors are the columns of $\mathbf{S}$.

Cindy: Since $\vec{\mathbf{w}}$ is a linear combination of the reaction vectors, does this mean we have shown that $\vec{\mathbf{w}}$ is in the column space $CS(\mathbf{S})$ of the stoichiometric matrix?

Question C28.3: Did Cindy get this right?

Theo: Exactly!

So how many reactions do we need?

Theo: So $\vec{\mathbf{w}}$ will also be a linear combination of any basis of $CS(\mathbf{S})$, in particular, of any basis of $CS(\mathbf{S})$ that we can form from some, but not necessarily all of the columns of $\mathbf{S}$.

Denny: Are you saying we can possibly get away with fewer than 4 reactions?

Theo: I wouldn't say it in this way, but essentially, yes.

That would depend on the size of the bases for $CS(\mathbf{S})$.

Denny: Isn't that the same as the rank $r(\mathbf{S})$?

Question C28.4: Did Denny get this right?

Theo: Exactly! When we observe a certain vector of net concentration changes, we can never be sure that more than $r(\mathbf{S})$ reactions actually occurred.

Question C28.5: But how do we find $r(\mathbf{S})$?

The rank of this stoichiometric matrix

Bob: We find $r(\mathbf{S})$ by performing some steps of a Gaussian elimination until we obtain a matrix in generalized row echelon form. We practiced this in Module 49.

$$\mathbf{S} = \begin{bmatrix} -1 & -1 & -1 & 0 \\ -2 & 0 & -1 & -1 \\ 2 & -2 & 0 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix} \xrightarrow{R2 \mapsto R2 - 2R1} \begin{bmatrix} -1 & -1 & -1 & 0 \\ 0 & 2 & 1 & -1 \\ 2 & -2 & 0 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix}$$

$$\xrightarrow{R3 \mapsto R3 + 2R1} \begin{bmatrix} -1 & -1 & -1 & 0 \\ 0 & 2 & 1 & -1 \\ 0 & -4 & -2 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix} \xrightarrow{R3 \mapsto R3 + 2R2}$$

$$\begin{bmatrix} -1 & -1 & -1 & 0 \\ 0 & 2 & 1 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 2 & 1 & -1 \end{bmatrix} \xrightarrow{R4 \mapsto R4 - R2} \begin{bmatrix} -1 & -1 & -1 & 0 \\ 0 & 2 & 1 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

The resulting matrix has 2 pivotal columns and 2 nonzero rows, and it follows that $r(\mathbf{S}) = 2$.

So, how many reactions could have occurred?

$$\mathbf{S} = \begin{bmatrix} -1 & -1 & -1 & 0 \\ -2 & 0 & -1 & -1 \\ 2 & -2 & 0 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix} \qquad r(\mathbf{S}) = 2 \qquad \vec{\mathbf{w}} = \begin{bmatrix} -3 \\ -4 \\ 2 \\ 2 \end{bmatrix}$$

Theo: So we cannot conclude, based on observing $\vec{\mathbf{w}}$ alone, that more than 2 reactions did actually occur.

Question C28.6: Can we infer that **at least** 2 reactions occurred?

Alice: Yes. Bob's $\vec{\mathbf{w}}$ is not a scalar multiple of any of the reaction vectors. Therefore, at least 2 reactions are needed to produce this observed net change.

I am wondering now though whether **any** 2 of the 4 reactions could have produced $\vec{\mathbf{w}}$ or whether we could narrow down the possibilities.

Why do 2 reactions always suffice here?

Theo: We cannot narrow down these possibilities. Any vector of net changes that is possible at all can be produced by any 2 among the 4 reactions.

Bob: Why?

Theo: Consider $\mathbf{S} = \begin{bmatrix} -1 & -1 & -1 & 0 \\ -2 & 0 & -1 & -1 \\ 2 & -2 & 0 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix}$

No two columns are scalar multiples of each other. Thus if we restrict our system to any two reactions, for example, to the first and the third reaction, the rank of the restricted

stoichiometric matrix $\mathbf{S}^- = \begin{bmatrix} -1 & -1 \\ -2 & -1 \\ 2 & 0 \\ 0 & 1 \end{bmatrix}$ would still be 2.

Why do 2 reactions always suffice? Completed.

Theo: Similarly, if we restrict the system to any other pair of 2 reactions, the stoichiometric matrix $\mathbf{S}^-$ of the reduced system would still have rank 2.

Bob and Frank: So what?

Theo: If we now take any vector of net changes $\vec{\mathbf{w}}$ that is possible for all 4 reactions, the rank of the extended matrix $r([\mathbf{S}, \vec{\mathbf{w}}])$ must still be 2, since $\vec{\mathbf{w}}$ is in $CS(\mathbf{S})$.

But then $r([\mathbf{S}^-, \vec{\mathbf{w}}])$ must also be 2, since it cannot exceed $r([\mathbf{S}, \vec{\mathbf{w}}]) = 2$ and it must be at least $r(\mathbf{S}^-) = 2$.

But this means that $\vec{\mathbf{w}}$ is a linear combination of the 2 columns of $\mathbf{S}^-$.

So we cannot rule out any given pair of 2 reactions.

Bob: Now I see. Thank you for explaining this to us!

What if some directions are energetically implausible?

Alice: But aren't you making a hidden assumption, Theo?

Theo: What do you mean?

Alice: Couldn't we perhaps rule out some pairs of reactions if we knew that they are energetically plausible only in one direction?

Theo: Oh! Yes, I have assumed that both directions are plausible for each reaction so that each reaction rate could be positive or negative.

Bob: I think we will explore Alice's question in Module 51; let's not discuss this further right now.

Frank: Good! Because I have another question: Isn't your example a bit weird, Theo? With 4 reactions among 4 chemicals, wouldn't the stoichiometric matrix typically have full rank—that is, rank 4—instead of a smaller rank?

Is Theo's example typical?

Theo: I don't know. I found this example in a textbook.

Alice: Your example is actually quite typical, Theo. Suppose we have a **closed** chemical reaction system with no removal of reaction products and no inflow of reactants. Then the rank of the stoichiometric matrix will always be less than the total number n of chemicals involved.

Frank: Why would that be?

Alice: Think what would happen if $r(\mathbf{S}) = n$. Then **every** vector would be a possible vector of net changes.

Question C28.7: How does this imply that $r(\mathbf{S}) < n$?

Alice: We could never see a vector of net changes with only positive elements, because then these reactions would produce reaction products without consuming reactants. This is not possible in a closed system of chemical reactions.

Take-home message

Consider a chemical reaction system with stoichiometric matrix $\mathbf{S}$.

A given vector $\vec{\mathbf{w}}$ can be a possible vector of net concentration changes only if it is a linear combination of the reaction vectors, that is, if $\vec{\mathbf{w}}$ is in the column space $CS(\mathbf{S})$ of the stoichiometric matrix.

Based on the observation of a given net concentration changes we can sometimes conclude that at least $r(\mathbf{S})$ of the reactions in the system did in fact occur, but we can never conclude, based on this observation alone, that more than $r(\mathbf{S})$ of the possible reaction did in fact occur.