MATH3200: APPLIED LINEAR ALGEBRA
SELF-STUDY AND PRACTICE MODULE 51: APPLICATIONS OF THE RANK TO SYSTEMS OF CHEMICAL REACTIONS

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This module is based on Lectures 27, 28 and Conversation 28.

Recall our example of a system of chemical reactions:
Reaction 1: $A + 2B \rightleftarrows 2C$
Reaction 2: $A + 2C \rightleftarrows 2D$
Reaction 3: $A + B \rightleftarrows D$
Reaction 4: $B + D \rightleftarrows 2C$

The stoichiometric matrix $\mathbf{S} = [\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4] = \begin{bmatrix} -1 & -1 & -1 & 0 \\ -2 & 0 & -1 & -1 \\ 2 & -2 & 0 & 2 \\ 0 & 2 & 1 & -1 \end{bmatrix}$ has rank $r(\mathbf{S}) = 2$,

and as we saw in Conversation 28, based on the observation of a particular vector $\vec{\mathbf{w}}$ of net concentration changes alone we cannot infer that *more than* 2 of these reaction actually occurred. Sometimes we can only infer that at least 1 of the reactions occurred. For example, consider the vector of net concentration changes $\vec{\mathbf{w}} = \begin{bmatrix} 5 \\ 5 \\ 0 \\ -5 \end{bmatrix} = -5\vec{\mathbf{v}}_3$ For this vector we can only infer that at least one reaction occurred, as $\vec{\mathbf{w}}$ could have been produced by reaction 3 alone, proceeding at net rate $k_3 = -5$. On the other hand, when we do observe this vector $\vec{\mathbf{w}}$ of net concentration changes, we cannot infer that only reaction 3 occurred, or even that reaction 3 occurred at all, since $\vec{\mathbf{w}} = -5\vec{\mathbf{v}}_3 - 5\vec{\mathbf{v}}_4$ could also have been produced by reactions 2 and 4 combined.

So far we have ignored the issue of whether the reactions are energetically plausible in both directions. This will not always be the case in real chemical reaction systems. For example, if the vector $\vec{\mathbf{w}}$ in the above example is produced by reaction 3 alone, then this reaction must occur at net rate $k_3 = -5$, so that the backward direction of reaction 3 must be energetically plausible.

Question 51.1: Consider our chemical reaction system and assume that each reaction is energetically plausible only in the forward direction. Assume that the vector of net concentration changes $\vec{\mathbf{w}} = \begin{bmatrix} -2 \\ -2 \\ 0 \\ 2 \end{bmatrix}$ has been observed. Is it possible that only reactions 1 and 2 did occur?

Question 51.2: Consider our chemical reaction system and assume that each reaction is energetically plausible only in the forward direction. Assume that the vector of net concentration changes $\vec{\mathbf{w}} = \begin{bmatrix} -2 \\ -2 \\ 0 \\ 2 \end{bmatrix}$ has been observed. Is it possible that only reactions 1 and 4 did occur?

An interesting special case is the situation where we observe no net change at all. Chemists then say that the system is *at chemical equilibrium.* This could happen if no reactions whatsoever occur, or if the reactions balance each other out, so that $\mathbf{S}\vec{\mathbf{k}} = \vec{\mathbf{0}}$, where $\vec{\mathbf{k}}$ is the vector of reaction rates. Note that in the terminology of Lecture 28 this means that the vector of reaction rates $\vec{\mathbf{k}}$ must then be in the null space $N(\mathbf{S})$ of the stoichiometric matrix. Thus, in general, we cannot deduce any of the net reaction rates k_i from observing a system at chemical equilibrium. However, if reactions have only one energetically plausible direction, we can sometimes deduce at least some of these net reaction rates.

Question 51.3: Consider our chemical reaction system and assume that each reaction is energetically plausible only in the forward direction. Assume that the vector $\vec{\mathbf{0}}$ of net concentration has been observed so that the system is at chemical equilibrium. What can we say about the vector $\vec{\mathbf{k}}$ of reaction rates?