MATH3200: APPLIED LINEAR ALGEBRA
SELF-STUDY AND PRACTICE MODULE 45B: APPLICATIONS OF LINEAR COMBINATIONS AND OF THE LINEAR SPAN TO SYSTEMS OF CHEMICAL REACTIONS: THE STOICHIOMETRIC MATRIX

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This module is based on Conversation 23 and gives you additional information about this material. In particular, we will introduce here the important concept of the *stoichiometric matrix* of a system of chemical reactions.

Recall that in Conversation 23 we considered systems of chemical reactions between certain *chemical species* that could be compounds or chemical elements.

We will write here this system in simplified symbols for the chemical species as

$$
\begin{array}{lc}
\text{(Reaction 1)} & A + 2B \rightleftarrows 2C \\
\text{(Reaction 2)} & A + 2C \rightleftarrows 2D \\
\text{(Reaction 3)} & A + B \rightleftarrows D \\
\text{(Reaction 4)} & B + D \rightleftarrows 2C
\end{array}
\tag{1}
$$

The double arrows in each reaction indicate that in theory it can (simultaneously) occur both in the *forward direction* (from left to right) and in the *backward direction* (from right to left). The chemical species on the left of each equation are called the *reactants* (of the forward reaction) and the species on right are called the *reaction products.*

Recall that the vector of concentrations (in moles per liter) at time t of all species will be written as

$$\begin{bmatrix} [A]_t \\ [B]_t \\ [C]_t \\ [D]_t \end{bmatrix}$$

The vector of *net changes* in concentrations between times $t = 0$ and times $t = 1$ is then

$$\vec{\mathbf{w}} = \begin{bmatrix} [A]_1 - [A]_0 \\ [B]_1 - [B]_0 \\ [C]_1 - [C]_0 \\ [D]_1 - [D]_0 \end{bmatrix}$$

In particular, if only the first reaction occurs in the forward direction with a net consumption of 1 mole per liter of the first reactant A, we get a net change of $\vec{\mathbf{v}}_1 = \begin{bmatrix} -1 \\ -2 \\ 2 \\ 0 \end{bmatrix}$

This vector is called the *reaction vector* of the first reaction. The reaction vectors for the other 3 reactions are:

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

In a system of chemical reactions, all reactions occur simultaneously. Let k_i denote the net rate at which reaction i occurs. Then the observed vector $\vec{\mathbf{w}}$ will be the linear combination of the reaction vectors with coefficients k_i. Thus in a system with 4 reactions as in our example, we will have

$$\vec{\mathbf{w}} = k_1\vec{\mathbf{v}}_1 + k_2\vec{\mathbf{v}}_2 + k_3\vec{\mathbf{v}}_3 + k_4\vec{\mathbf{v}}_4. \tag{2}$$

Note that $k_i > 0$ signifies that the forward direction of the reaction dominates, $k_i < 0$ signifies that the backward direction of the reaction dominates, and $k_i = 0$ signifies that the reaction does not occur or that the forward and backward direction exactly cancel each other our.
Thus a given vector $\vec{\mathbf{w}}$ can be a vector of net changes for a given reaction system if, and only if, $\vec{\mathbf{w}}$ is in the linear span of the reaction vectors. In our example this would mean that $\vec{\mathbf{w}}$ would need to be in $span(\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4)$.
The matrix whose columns are the reaction vectors for a given chemical reaction system is called the *stoichiometric matrix* of this system and will be denoted here by $\bar{S}$. While there is no universal agreement among chemists whether the reaction vectors should be written as the rows or the columns of the stoichiometric matrix, in this course *we always will write them as the columns of* $\mathbf{S}$. The reason is that when we use this convention, we can express the vector $\vec{\mathbf{w}}$ of net changes as the product of $\mathbf{S}$ with the vector $\vec{\mathbf{k}}$ of net reaction rates:

$$\mathbf{S}\vec{\mathbf{k}} = \vec{\mathbf{w}}. \tag{3}$$

In particular, for a system with 4 reactions like in our example, (3) becomes:

$$\mathbf{S} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \\ k_4 \end{bmatrix} = \vec{\mathbf{w}}. \tag{4}$$

Notice that for our definition of $\mathbf{S}$, Equations (2) and (4) are two different ways of expressing the exact same thing. Moreover, notice that a given vector $\vec{\mathbf{w}}$ can be a vector of net changes for a given reaction system if, and only if, the corresponding linear system (3) is consistent.

Question 45.4: Find the stoichiometric matrix $\mathbf{S}$ for the system in our example.

Question 45.5: Recall that in Conversation 23 Frank said that the vector $\vec{\mathbf{w}} = \begin{bmatrix} 3 \\ -4 \\ 0 \\ 2 \end{bmatrix}$

could not be a vector of net changes for the system in our example. Was he right? How would you use the terminology introduced in this module to determine the answer?