# Conversation 23: Applications of Linear Combinations and of the Linear Span to Systems of Chemical Reactions

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MATH 3200: Applied Linear Algebra

# Linear combinations and the linear span: Review of the definitions

**Definition**

A vector $\vec{\mathbf{w}}$ is a *linear combination* of vectors $\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \ldots, \vec{\mathbf{v}}_n$ if there exist scalars $d_1, d_2, \ldots, d_n$ such that

$\vec{\mathbf{w}} = d_1\vec{\mathbf{v}}_1 + d_2\vec{\mathbf{v}}_2 + \cdots + d_n\vec{\mathbf{v}}_n$.

The *linear span* of a set of vectors $\{\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \ldots, \vec{\mathbf{v}}_n\}$ is the set $span(\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \ldots, \vec{\mathbf{v}}_n)$ of all linear combinations of these vectors..

In Conversation 22 we saw an example of applications to foraging bees.

# Can we look at an example for grown-ups?

**Frank:** This example was all very cute, but in a college course for engineering students we should really be looking at some example for grown-ups. A real example from science or engineering.

**Theo:** I recently read about a great example from chemistry in the book

Gerhard Just *et al.* (1988) *Mathematik für Chemiker. (Mathematics for Chemists.)* 3rd edition. VEB Deutscher Verlag für Grundstoffindustrie.

**Denny:** Showoff!!

**Frank:** Seems our instructor is trying to promote his family business here. Probably a conflict of interest. Some university committe should investigate!

**Cindy:** But perhaps it's a good example?

**Bob:** So what is it?

# Theo's example

**Theo:** Consider a system of chemical reactions for the species oxygen $O_2$, carbon monoxide $CO$, carbon dioxide $CO_2$ and carbon $C$. Then the only possible reactions are

$$O_2 + C \rightleftarrows CO_2 \qquad O_2 + 2C \rightleftarrows 2CO$$

$$O_2 + 2CO \rightleftarrows 2CO_2 \qquad C + CO_2 \rightleftarrows 2CO$$

**Denny:** What's a "system of chemical reactions"?
And what are "chemical species"?

**Theo:** A chemical species could be either a compound, like carbon dioxide $CO_2$, or a chemical element, like carbon $C$.
In a chemical reaction like $O_2 + C \longrightarrow CO_2$ some of these species combine to form more complex compounds; in a chemical reaction like $CO_2 \longrightarrow O_2 + C$ some of them split up into simpler species.

**Denny:** So the "system" would be just a bunch of these chemical reactions that can occur between a bunch of chemicals?

**Theo:** I would not say it this way, but basically, yes.

# Forward and backward reactions

**Bob:** On the previous slide you wrote $O_2 + C \overset{\longrightarrow}{\longleftarrow} CO_2$ in one place, but later $O_2 + C \longrightarrow CO_2$ and $CO_2 \longrightarrow O_2 + C$.
Which notation is correct?

**Theo:** The reaction $O_2 + C \longrightarrow CO_2$ is the burning of carbon. We will call it here the *forward reaction* or the *forward direction.* In chemistry it is assumed that for every reaction there is also a reaction that goes in the opposite direction. That would be $CO_2 \longrightarrow O_2 + C$ or $O_2 + C \longleftarrow CO_2$. When we write a system of chemical reactions we combine these two reactions into one by using double arrows. The one for which the arrow points to the left is called the *backward reaction* or *backward direction.*

**Alice:** But in your example of carbon burning, the forward reaction happens quite a lot and the backward reaction $O_2 + C \longleftarrow CO_2$ doesn't seem to happen, or else there would be no problem of global warming!

**Theo:** The backward reaction is chemically possible, so we need to include it in the system. But since burning releases energy, going backwards would consume a lot of energy. Thus the backward reaction does not readily occur. We can say that it is *energetically implausible.*

# Let's simplify our notation

$$O_2 + C \rightleftarrows CO_2 \qquad O_2 + 2C \rightleftarrows 2CO$$
$$O_2 + 2CO \rightleftarrows 2CO_2 \qquad C + CO_2 \rightleftarrows 2CO$$

**Cindy:** I'm not good a chemistry and all these symbols like $CO_2$ are very confusing. Can we use simpler ones?

**Theo:** Since this is a mathematics course, we can basically ignore what particular species the symbols represent. From now on, we can just consider a system with species named $A, B, C, D$:

$$A + 2B \rightleftarrows 2C \qquad A + 2C \rightleftarrows 2D$$
$$A + B \rightleftarrows D \qquad B + D \rightleftarrows 2C$$

**Frank:** Seems you scrambled up your reactions here.

**Bob:** We can unscramble them at home.

So what do we want to know about this system?

**Theo:** Suppose chemists know that the following reactions could in principle occur:

$$A + 2B \rightleftarrows 2C \qquad A + 2C \rightleftarrows 2D$$
$$A + B \rightleftarrows D \qquad B + D \rightleftarrows 2C$$

However, suppose they do not know **which** of these reactions actually occur and that we want to figure this out by observing how the concentrations change over time.

**Cindy:** Should we think of concentrations as vectors or scalars?

**Theo:** Good question! For each individual species, the concentration (for example, in moles per liter) will be denoted by putting the symbol of that species into square brackets: $[A], [B], [C], [D]$. But we will consider here the concentrations for all species, and we will write them as column vectors: $[[A], [B], [C], [D]]^T$.

# Net change of concentrations

**Bob:** You mentioned "net change." Wouldn't that mean that these concentrations change over time?
So that we should write $[A](t)$ instead of $[A]$, and so on?

**Theo:** You are right, we need to bring in time $t$, in suitable units.

**Cindy:** But all these brackets in Bob's notation will be so confusing!
Can we write $[A]_t$ instead of $[A](t)$?

**Theo:** Yes we can. Now suppose you take measurements at times $t = 0$ and $t = 1$ and observe concentration vectors
$[[A]_0, [B]_0, [C]_0, [D]_0]^T = [15, 17, 10, 22]^T$ and
$[[A]_1, [B]_1, [C]_1, [D]_1]^T = [18, 13, 10, 24]^T$ at these times.
Then the *net change* in concentrations is the vector:

$$\begin{aligned}\vec{\mathbf{w}} &= [[A]_1 - [A]_0, [B]_1 - [B]_0, [C]_1 - [C]_0, [D]_1 - [D]_0]^T \\ &= [3, -4, 0, 2]^T.\end{aligned}$$

**Bob:** So, when we observe this vector of net changes, can we then say that between times $t = 0$ and $t = 1$ some of the reactions have produced a total of 3 moles per liter of $A$, 2 moles per liter of $D$, have consumed 4 moles per liter of $B$, and no reaction that involves $C$ has occurred at all?

**Question C23.1:** Did Bob get this right?

**Not quite.**

**Theo:** Since several reactions may occur simultaneously, some of them may produce a given chemical, while others consume it. This is why we call $\vec{\mathbf{w}}$ the vector of **net** changes.

**Cindy:** So, in your example, the net change $[C]_1 - [C]_0$ might have been observed because the production of $C$ by some reactions and consumption of $C$ by other reactions canceled each other out?

**Theo:** Exactly! The net change represents the difference between total production and total consumption.

**Frank:** But is it **even possible** to observe $\vec{\mathbf{w}} = [3, -4, 0, 2]^T$ as a vector of net changes in the example of a system that you gave us? I strongly doubt it.

**Theo:** Excellent question! This is exactly where I wanted to go with my example.

# A reaction vector

**Theo:** Let us assume for a moment that we have just one reaction

1. $A + 2B \rightleftarrows 2C$

among our 4 chemical species $A, B, C, D$. If the net change in $[A]$ over a certain time interval is consumption of one mole per liter, then the reaction would simultaneously consume 2 moles per liter of $B$ and produce 2 moles per liter of $C$, while the concentration of $D$ remains unchanged.

Thus the observed net change must be $\vec{\mathbf{v}}_1 = [-1,\ -2,\ 2,\ 0]^T$.

This vector is called the *reaction vector* for the first reaction.

**Question C23.2:** What vectors of net changes could we possibly observe over time in this system that is comprised of only the first reaction?

**Theo:** If only this first reaction can occur and both the forward and backward reaction are energetically plausible, we could observe all vectors of the form $k\vec{\mathbf{v}}_1 = k[-1,\ -2,\ 2,\ 0]^T = [-k,\ -2k,\ 2k,\ 0]^T$

where $k$ is a real number that represents the *net reaction rate.*
Here $k > 0$ if the forward reaction dominates; and $k < 0$ if the backward reaction dominates.

# What if only one direction is energetically plausible?

**Cindy:** So, when only the forward reaction is energetically plausible, as you would say, then we could only get net change vectors $k\vec{\mathbf{v}}_1$ for $k > 0$, and when only the backward reaction is energetically plausible, then we could only get net change vectors $k\vec{\mathbf{v}}_1$ for $k < 0$, right?

**Question C23.3:** Did Cindy get this right?

**Almost.**

**Theo:** We also can get no change at all, because we assume only that the reaction is possible, not that it will actually occur. To be completely precise:

- When only the forward reaction is energetically plausible, we can only have $k \geq 0$, and
- when only the backward reaction is energetically plausible, we can only have $k \leq 0$.

# Vectors for each reaction

**Theo:** We can construct similar reaction vectors $\vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4$ for the other three reactions in the system

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

Each of the 4 reaction vectors $\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4$ can make a contribution to the vector $\vec{\mathbf{w}}$ of net concentration changes, and these contributions add up.

**Denny:** Oh I see! Then $\vec{\mathbf{w}} = k(\vec{\mathbf{v}}_1 + \vec{\mathbf{v}}_2 + \vec{\mathbf{v}}_3 + \vec{\mathbf{v}}_4)$ for some $k$.

**Question C23.4:** Did Denny get this right?

**Theo:** Not necessarily. In general, the reactions may proceed at different rates. But $\vec{\mathbf{w}}$ is always a linear combination $\vec{\mathbf{w}} = k_1\vec{\mathbf{v}}_1 + k_2\vec{\mathbf{v}}_2 + k_3\vec{\mathbf{v}}_3 + k_4\vec{\mathbf{v}}_4$ of the reaction vectors, where the coefficients are the net rates $k_1, k_2, k_3, k_4$ of the individual reactions.

# How about Frank's question?

**Alice:** Can you remind us of your question, Frank?

**Frank:** I said I seriously doubt that it is even possible to observe $\vec{\mathbf{w}} = [3, -4, 0, 2]^T$ as a vector of net changes in the system of the previous slide. You can call this a question, if you want.

**Theo:** You were in effect asking whether $\vec{\mathbf{w}} = [3, -4, 0, 2]^T$ is a linear combination of the rection vectors $\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4$ for this system.

**Frank:** Are you saying, Theo, that I was asking whether $\vec{\mathbf{w}} = [3, -4, 0, 2]^T$ is in the linear span $span(\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \vec{\mathbf{v}}_3, \vec{\mathbf{v}}_4)$?

**Theo:** Very well put, indeed.

**Frank:** (Laughs) That's a good one!

**Denny:** So was Frank right with his doubt, or not?

**Bob:** I think we are supposed to figure this out ourselves in Module 45. Let's call it quits for today.

# Take-home message

This conversation illustrates how the concepts of linear combination and linear span can be applied to the study of systems of chemical reactions.

We defined *vectors of net concentration changes* $\vec{\mathbf{w}}$ and *reaction vectors* $\vec{\mathbf{v}}_1, \dots, \vec{\mathbf{v}}_n$ for the individual reactions in a system.

The vector $\vec{\mathbf{w}}$ of net concentration changes is always a linear combination

$\vec{\mathbf{w}} = k_1\vec{\mathbf{v}}_1 + k_2\vec{\mathbf{v}}_2 + \dots + k_n\vec{\mathbf{v}}_n$ of the reaction vectors, where the coefficients are the *net rates* $k_1, k_2, \dots, k_n$ of the individual reactions.

In this terminology, as long as both the forward and backward direction of each reaction are energetically plausible, a given vector $\vec{\mathbf{w}}$ is a possible vector of net concentration changes for a given system if, and only if, $\vec{\mathbf{w}}$ is in the linear span $span(\vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2, \dots, \vec{\mathbf{v}}_n)$ of the reaction vectors.