

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

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

The *linear span* of a set of vectors  $\{\vec{v}_1, \vec{v}_2, \dots, \vec{v}_n\}$  is the set  $\text{span}(\vec{v}_1, \vec{v}_2, \dots, \vec{v}_n)$  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 committee 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



**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  $O_2 + C \rightarrow CO_2$  some of these species combine to form more complex compounds; in a chemical reaction like  $CO_2 \rightarrow O_2 + C$  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  $O_2 + C \rightleftharpoons CO_2$  in one place, but later  $O_2 + C \longrightarrow CO_2$  and  $CO_2 \longrightarrow O_2 + C$ .

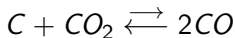
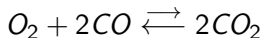
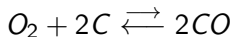
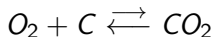
Which notation is correct?

**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!

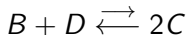
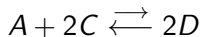
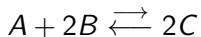
**Theo:** The backward reaction is chemically possible, so we need to include it in the system. But since burning releases energy, going backwards would consume a lot of energy. Thus the backward reaction does not readily occur. We can say that it is *energetically implausible*.

## Let's simplify our notation



**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  $A, B, C, D$ :



**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?

# Some questions chemists ask

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



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

$$[[A]_0, [B]_0, [C]_0, [D]_0]^T = [15, 17, 10, 22]^T \text{ and} \\ [[A]_1, [B]_1, [C]_1, [D]_1]^T = [18, 13, 10, 24]^T \text{ at these times.}$$

Then the *net change* in concentrations is the vector:

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

**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?



# Net change

**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  $\vec{w}$  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?

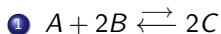
**Theo:** Exactly! The net change represents the difference between total production and total consumption.

**Frank:** But is it **even possible** to observe  $\vec{w} = [3, -4, 0, 2]^T$  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



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  $\vec{v}_1 = [-1, -2, 2, 0]^T$ .

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  $k\vec{v}_1 = k[-1, -2, 2, 0]^T = [-k, -2k, 2k, 0]^T$

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  $k\vec{v}_1$  for  $k > 0$ , and when only the backward reaction is energetically plausible, then we could only get net change vectors  $k\vec{v}_1$  for  $k < 0$ , right?

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

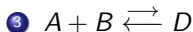
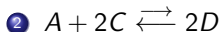
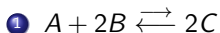
**Almost.**

**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  $\vec{v}_2, \vec{v}_3, \vec{v}_4$  for the other three reactions in the system



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

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

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

**Theo:** Not necessarily. In general, the reactions may proceed at different rates. But  $\vec{w}$  is always a linear combination

$\vec{w} = k_1\vec{v}_1 + k_2\vec{v}_2 + k_3\vec{v}_3 + k_4\vec{v}_4$  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  $\vec{w} = [3, -4, 0, 2]^T$  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  $\vec{w} = [3, -4, 0, 2]^T$  is a linear combination of the reaction vectors  $\vec{v}_1, \vec{v}_2, \vec{v}_3, \vec{v}_4$  for this system.

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

**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*  $\vec{w}$  and *reaction vectors*  $\vec{v}_1, \dots, \vec{v}_n$  for the individual reactions in a system.

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

$\vec{w} = k_1\vec{v}_1 + k_2\vec{v}_2 + \dots + k_n\vec{v}_n$  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  $\vec{w}$  is a possible vector of net concentration changes for a given system if, and only if,  $\vec{w}$  is in the linear span  $\text{span}(\vec{v}_1, \vec{v}_2, \dots, \vec{v}_n)$  of the reaction vectors.