FDSC400, Part 1. Kinetics

Supplemental reading: Chapter 17.3 of the Fennema text offers several ways to understand the changes in foods with time and temperature. In this course we will focus only on the one closest to classical chemical kinetics. The basic theories of kinetics are covered in adequate detail in most general chemistry tests.

1. Introduction

The application of kinetics provides a scientific and quantitative understanding of common sense. No one expects foods to last forever – bread is fresh for a few days then becomes progressively worse, a steak cooked for a minute will be rare but after ten minutes will be well done. Out experience teaches us that time and temperature are crucial factors affecting the quality of foods. If we can understand a change mathematically we can predict how changes in our process will affect the quality of a product. This section will be concerned with how the properties of food change with time and how we can use a quantitative understanding of this process to predict shelf life and optimal storage conditions. A key concept here is we can be very vague about the reaction we are talking about yet be very precise about how it proceeds. We will often define a parameter as food quality, which can be any number of factors or combination of factors. This could be a real chemical reaction such as the reaction of fat with oxygen but it might also be physical- like crunchiness in a cookie or formation of visible defect, or most probably consumer perception - sensory scores or a combination of factors. Later on in the course we will encounter some of the important reactions that determine food quality and the approaches studied here will help govern how they contribute to the success or failure of a product.

On completing this section you should be able to:

1. Identify and provide examples of kinetic changes in foods
2. Understand and be able to properly use the terms reaction rate and reaction order
3. Use rate equations to predict the changes in food as a function of time
4. Use the Arhennius equation to predict changes in rate with respect to temperature
5. Use rate equations and the Arhennius equation together to model the effects of time and temperature on a process.
6. Be able to design and understand the limitations of an accelerated shelf-life test.

2. Rate Equations

A chemist would start a description of chemical kinetics by designing an imaginary reaction where A is converted to B:

$$A \rightarrow B$$

You could then calculate how the concentration of A decreases and B increases as the reaction progresses. In chemistry it is relatively easy to provide examples of what A and B are (e.g., H_2O_2 reacts to form water and half a molecule of oxygen). If we are concerned with the organic chemistry going on in foods we could do something similar. For example during pasteurization vitamin C is thermally destroyed and studying the kinetics of the reaction would teach us something about how the nutritional quality of the drink would change. In another example we might be interested in how spinach looses its green color during steaming. If we know the green color of spinach is due to the pigment chlorophyll then we can use measurements of chlorophyll concentration as a chemical proxy for color. Here [chlorophyll] is not interesting in itself, but only as it tells us the color of the plant food. However, in other cases we might have no idea what chemical reaction is responsible for the changes in food quality we are interested in. For example cornflakes sometimes become soft if they are stored too long, coffee stored hot might become bitter and loose its characteristic flavor, meat roasted for long periods of time might become dry. In all of these cases we cannot point to a chemical reaction as responsible for the changes we are interested in. We can however say that some sort of reaction must have taken place and so write a general expression:

$$\text{Reagents} \rightarrow \text{Products}$$

We can define [reagents] and [products] in whatever way is convenient or us, in the earlier chemical examples this would have been simply [vitamin C] and [chlorophyll] but in the later food examples it could be instrumental measurement of cornflake texture, sensory score of coffee quality, of change in mass of the meat roast as it dries out in the oven. The later examples are not defined chemical reactions but can be measured and will change as the reaction proceeds. We will use mathematical models to predict how food will respond to different conditions and use that to estimate a maximum shelf-life or optimum processing time

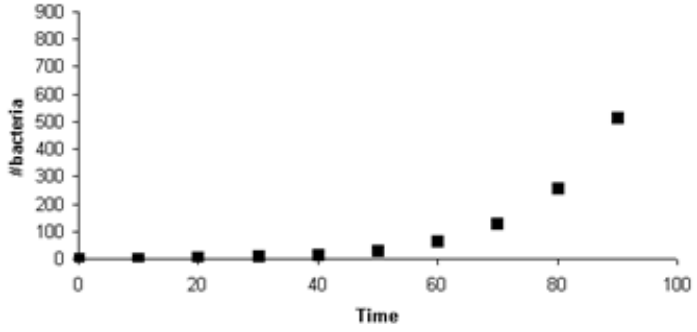
If reagents are being converted to products then the rate of loss of one is equal to the rate of gain of the other (note Products are always shown as Positive):

$$-\frac{dR}{dt} = \frac{dP}{dt}$$

The rate of the reaction depends on the mechanism. To illustrate this imagine we were modeling the process of bacterial growth. Simply put, to make a new bacterium the parent splits into two

Bacterium → Bacterium + Bacterium

Typically a bacterial like *e. coli* can do this every 30 mins. So one bacterium at time zero would lead to
At 30 min 2 bacteria,
At 60 min 4 bacteria
At 90 min 8 bacteria
At 120 min 16 bacteria
At 150 min 32 bacteria etc.



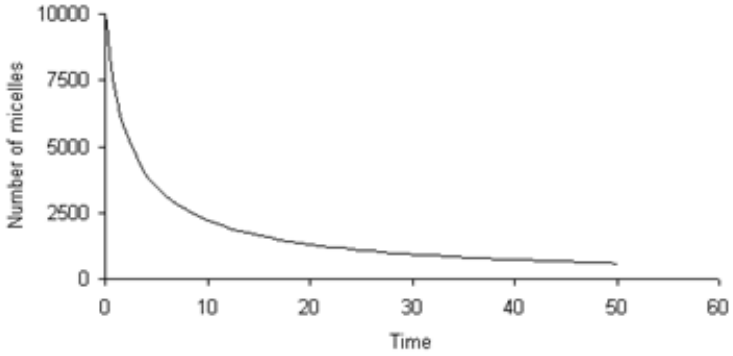
The number of bacteria is increasing with time but so is the rate of increase. In the first 30 min the change in the number of bacteria is 1 so dP/dt is 1/30 min^{-1}. In the second 30 min it is 2/30 min^{-1}, then 4/30 min^{-1} and so on. Essentially the same "reaction" is occurring but dP/dt is progressively increasing[1]. We can easily show that the rate is proportional to the number of bacteria there and so

Rate = k [Reagents]

Where k is a proportionality constant, the rate constant. We say this is a first order reaction because [Reagents] is raised to the power 1 (not shown in the equation). The higher the value of k the faster the reaction proceeds. The rate constant defines the proportion of reagents that will react in a given time. The absolute numbers that react depend on how many are there.

Consider a second example. During yogurt manufacture we are interested in making the milk proteins set to form a gel. The proteins we are concerned about are caseins, which naturally form into large (~1 μm) clumps of many protein molecules known as casein micelles. To make yogurt, the milk is fermented with lactic acid bacteria that convert the milk lactose to lactic acid and the pH drops. When the pH gets low enough the casein micelles begin to aggregate and this is the first step in the formation of the yogurt gel. Expressed this way the reaction we are concerned with is

Casein micelle + casein micelle → casein dimer



The rate of the reaction is -d[casein micelle]/dt or d[casein dimer]/dt. In order to react the two micelles must collide, the rate of a binary collision is proportional to concentration squared. The

[1] Obviously this is just a cop-out for doing the calculus of the process properly!

chance of a casein micelle hitting another casein micelle is proportional to the number of casein micelles available

i.e., Rate of a given micelle hitting another one $\propto$ number available

But each micelle has this chance of colliding so the total number of collisions is this times the total number of micelles available:

i.e., total rate of collisions $\propto$ number available x number available

or

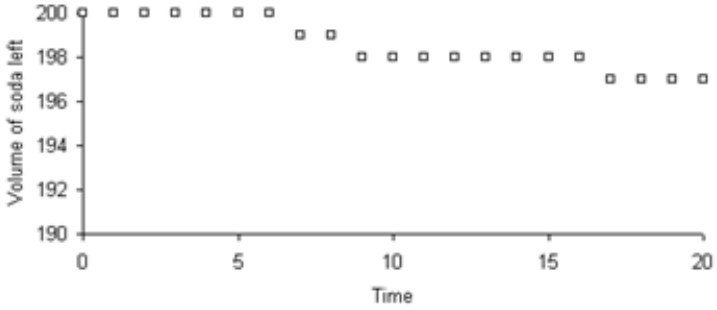
$$\text{Rate} = -d[\text{micelles}]/d\,(\text{time}) = -k[\text{micelles}]^2$$

Where k is a rate constant. The order of the reaction is here 2 because it is proportional to the rate raised to the second power. Note also the unit of k depends on the order of the reaction, absolute rate is always <concentration> <time> $^{-1}$, but the rate constant is in units <concentration>$^{\text{order-1}}$ <time>$^{-1}$.

Consider a third, more trivial example – the change in volume of soda in a drinks dispenser in a convenience store. We could write the change as a "reaction"

Soda in container → Soda dispensed

With a rate equal to –d[soda in container]/d [time] (here we should use volume of soda in container rather than the concentration brackets "[]" but we will cautiously maintain the convention for consistency). We can easily measure the volume of the container and would expect a typical plot to be similar to that shown in the Figure. Note that the rate is not constant (customers either take a full cup or nothing so it appears as a stepwise function), nor are the cups poured at a regular rate, however we can see that the overall rate of decrease in volume is approximately linear with time. The change in soda volume in a given time depends on the flow of customers through the store and how thirsty they are not on how much soda is in the container. So the rate is:



$$\text{Rate} = -d[\text{soda in container}]/d\,[\text{time}] = -k$$

The rate is constant (=-k) and the reaction is zeroth order with respect to soda volume, i/e/. the possibility of selling a soda doesn't depend on how much is available..

Building off the logic of the previous paragraph we could hypothesize that k could be expressed as a function of the rate of customers entering the store times their average thirstiness but not on the volume of soda, i.e.,

k=k' x <rate of custom> x <% thirstiness>

So we have identified three separate formulae of the rates of reaction with different order. Combining them we can see that in general:

Rate= -k[reagents]^n=k[products]^n

Where k is the rate constant of the reaction and n is the order (=0-2). Finally consider a truly complex reaction, for example the formation of brown color on the crust of a loaf as it bakes. The color is due to pigments known as melanoidins forms from the reaction between amines (from proteins) and reducing sugars (i.e., those with a free aldehyde group). A simplified mechanism of the reaction is given in the Hodge scheme (see later in the notes for a more complete treatment of this famously complex reaction)

Reducing sugar + Amine →Intermediates→ Brown pigment

But that would clearly be a gross oversimplification ignoring the potential for cross reactions, catalytic intermediates, non-pigmented products etc. In fact there are many pathways and competing reactions could lead to the colored product we are interested in and in all cases multiple reaction steps are involved, each with different rates and orders. In steady state, we can still say: Rate =k[brown color]^n, where k is the rate of a composite reaction but because it is a composite reaction we need no-longer assume n has an integer value[2].

The equation Rate= -k[reagents]^n is a start but not a really that helpful. It tells us that if we know two parameters (k and n) we can calculate the rate of change of something. However, rate of change is not what we need to know but rather the absolute amount as a function of time (e.g., how much vitamin C is there after 10 min cooking or how much soda will be left by the end of the day). We need to integrate the rate equation, so if

$$\text{Rate}= -\frac{dR}{dt} = \frac{dP}{dt} = k[P]^n$$

Then: $$P = \int_t k[P]^n \, dt$$

Starting with a trivial example, zeroth order reactions, Rate=d[P]/dt=k, therefore

[2] In the context of this class we will not be concerned with non-integer reaction orders, but you should be aware under what circumstances they may exist.

$$P = \int_t k.dt = kt$$

or [R]=[R_0]-kt, where R_0 is the starting concentration of reagents. So in the soda example if we know k is 10 l hr^{-1}, we can say that after 2 hours 20 liters of soda will have been dispensed.

Life gets slightly more complicated for the higher order reactions. For the first order case Rate=d[R]/dt=-k[R] so

$$\int \frac{1}{R} dR = -\int k.dt$$
$$\ln(R) + C = -kt$$

where C is an integration constant. Knowing that at time zero, R is at a maximum starting value (=R_0) we can say:

$$\ln(R_0) + C = -k \times 0$$
$$C = -\ln(R_0)$$

substituting:

$$-\ln\left(\frac{R}{R_0}\right) = kt$$
$$R = R_0 \exp(-kt)$$

This equation implies that the logarithm of the relative extent of the reaction (R/R0) should be proportional to time. This is easy to verify graphically. There are also standard integrals for second order and non-integer reactions (see Table 1 on page 1018 of the Fennema text). Once we know order and rate constant we can use these equations to calculate concentration as a function of time.

From the form of the equations we can see that a plot of [R] with time should give a straight line when plotted against time only for a zeroth order reaction, ln (R/R_0) should give a straight line for a first order reaction. By plotting our data in this manner we can identify the order of the reaction (which plot gives the best straight line) and the rate constant (what is the slope of the straight line plot).

Question 1: Rate Constants.

1. The quality of a bagged salad product was judged by a consumer sensory panel and ranked from 10=excellent to 1=revolting. The average sensory score of the products is shown in the data set provided. What is the apparent reaction order of the salad deterioration process? What is the rate constant of the process? If salads became inedible at a sensory score less than 3, how long could you keep this product?

2. Aspartame is an artificial sweetener used in drinks. It breaks down during the storage of the product leading to a loss of sweetness. Assuming the reaction is first order, use the data provided to calculate the rate constant of the process and calculate the time for the concentration of aspartame to reach 50% of its initial value.
3. The rate constant for bacterial growth is 0.1 day^{-1}. If the likely number of a given bacteria needed to cause an infection is 1,000,000 how long would you store a food with an initial load of (a) 1 bacteria, (b) 1000 bacteria?

Question 2: Frying Burgers.

1. Beef burgers loose mass as they are fried. Why? Assume the reaction is first order. Use the data provided to calculate the rate constant.

Question 3: Toxin Destruction

1. The rate constant for the destruction of an endogenous toxin during the cooking of shellfish is 0.05 (unit depends on order – assume time unit to be minutes). Assuming the initial toxin content is 15 mg kg^{-1}, calculate the toxin content after 1 and 50 min cooking assuming the reaction is 0, 1 or 2nd
2. Based on your previous answer (and making whatever additional calculations and plots you find helpful), how long would you have to run your experiment to confidently calculate the order of the reaction? Why?

3. Temperature Dependency

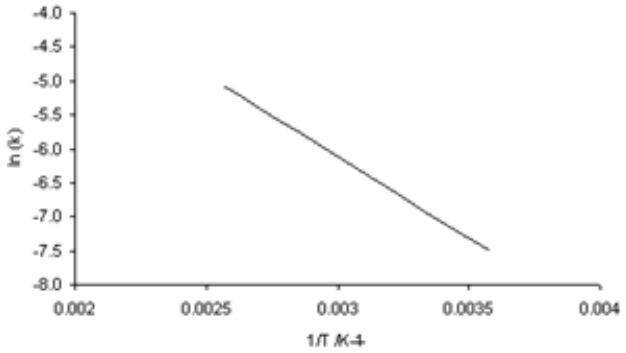
The rate of chemical reaction depends on the conditions (e.g., temperature, pH, presence of catalysts or inhibitors). It would be helpful to incorporate these terms into our rate equations so we could extend them to conditions other than those where measurements were made. The most successful and general approach to this problem is the use of Arhennius kinetics which relate the rate constant to temperature:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

where k is the rate at absolute temperature T, E_a is the activation energy of the reaction (a measure of how much faster the reaction goes when heated), R is the gas constant (=8.3 J. K^{-1} mol^{-1})and k_0 a constant (the rate at a reference temperature). This equation tells us that as T increases, the term in brackets decreases, so the left hand side of the equation increases, so the right hand side of the equation increases. Meaning as temperature increases so does the reaction rate – the equation makes qualitative sense. It is easier to deal with an equation containing an exponential by taking logs and turning it into a linear expression. In this case taking the natural log of both sides:

$$\ln k = \ln k_0 - E_a/R \cdot 1/T$$

Compare this equation to the equation of a straight line, y=C-Mx. If we plot ln k against 1/T we would expect a straight line with y-intercept of k_0 and a slope of $-E_a/R$. It is then possible to calculate the constants by fitting a best-fit line to the data and then calculate the rate constant at any temperature. Knowing the rate constant and assuming the order of the reaction is unchanged by the change in temperature the progression of the reaction at a different temperature can then be calculated using one of the rate equations developed earlier.



Question 4: Degradation Kinetics of Chlorophyll in Peas as a Function of pH

Chlorophyll is the important green pigment in vegetables, including peas. Three are in fact two almost identical compounds (chlorophyll a and b) and both break down during food processing to leave an unpleasant olive green color. It is important to optimize the cooking conditions to maximize chlorophyll, and hence color, retention. However, we do not need to know the mechanism of chlorophyll degradation in order to design a model for the color loss in peas. (If you are interested the chemistry of chlorophyll is clearly explained in section 12.2.2 in Fennema). Read the paper provided in class and answer the following questions.

1. What precision in temperature and pH is the reactor developed by Ryan-Stoneham capable? How does the reactor automatically increase the pH of a solution?

2. In Figures 3-5, why are the authors confident a first order reaction is proceeding? How does the rate of chlorophyll loss change with pH? Temperature?

3. In Figure 7a, how can you be certain the activation energy is independent of pH? (2 points)

Question 5: Cooking meat.

1. The rate constant for brown color formation on the surface of grilled meat was calculated as a function of temperature. Plot the data as an Arhennius plot and calculate the activation energy for the browning reaction.

Temp /°C	100	120	140	160	180	200

Rate constant /h^{-1}	0.001591	0.001875	0.002174	0.002487	0.002811	0.003146

2. The rate constant for the loss of vitamin B on cooking meat is 0.5 h^{-1} at 100°C. The activation energy for the reaction is 18 $kJ.mol^{-1}$. What would be the rate constant of degradation at 450 F?
3. Plot the rate-temperature function for vitamin loss on the same axis as used for the vitamin loss data above. Assume you wanted to make a brown product with a high vitamin content – use this Figure to explain what cooking temperature would you choose and why?

4. Accelerated Shelf Life Testing

In defining equations to describe the way foods change over time we have created a model for the process. As we saw in the soda example the model need not be perfect but should hopefully give a good approximation of how the process will proceed over time. One value to this is we can now predict how a system will change without doing experiments. Within the time range we have measured we know the model fits the data well so we have great confidence in the model, but to make a prediction outside this range we will run into problems of extrapolation. For a simple and well characterized chemical reaction this is often OK but may be less reliable in a food. Furthermore food systems are such complex materials full of uncharacterized catalysts and inhibitors of reactions it is hard to use a literature value of rate constant to make a prediction. We must often rely on our own measurements of the rate constant to estimate the time course of the reaction.

Measuring a rate constant is relatively easy provided you have good experimental data. For that we need a good measurable change in the parameter of interest (i.e., many times larger than the precision of the experimental error) so we can (i) recognize the shape of the function and decide an appropriate order for the reaction, and (ii) fir a rate equation to the data and measure the rate constant. If the reaction is very slow (e.g., the rate of lipid oxidation in dried beef) we could calculate the rate constant only after making measurements over several years. This approach clearly cannot work in product development.

Instead we must find a way to accelerate the reaction (usually by heating) to get a measurable rate constant (and order) in a reasonable time then calculate how much more slowly the reaction proceeds at a lower temperature. Thus the experimental protocol is

(i) Calculate the rate of the reaction at several elevated temperatures by measuring [property] vs. time and fitting an appropriate rate equation.

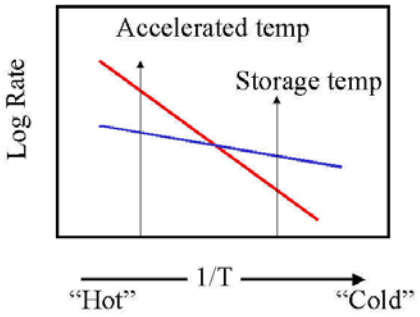
(ii) Plot the rate data, ln k, vs reciprocal absolute temperature, 1/T in an Arhennius plot. Fit a straight line to the data and extrapolate to the temperature the product is actually going to be stored. Read off the rate of the reaction at that temperature.

(iii) Plug the rate into a rate equation to predict how [property] changes with time at the storage temperature. We have predicted the shelf life of a product in less time than it would take for the shelf life to degrade naturally, i.e., this is an **accelerated shelf life test**.

There are substantial problems with this approach and it must be treated with caution. First amongst these is to question whether the reaction you are studying at the elevated temperatures is the same reaction taking place at the storage temperature? For example:

- Bacterial growth is a substantial issue in vegetables stored at warmer temperatures while enzymatic degradation is important at low temperatures
- Ice coarsening limits the shelf life of ice cream at –10°C but clearly not at elevated temperatures

A more systematic explanation of this problem is to suggest there are two reactions with different activation energies and reaction rates at a given (high) temperature. During the accelerated tests we would measure the "red" reaction (because that is what occurs faster), extrapolating this would give us no idea of the situation at lower temperatures when the "blue" reaction would dominate. (If you labeled blue as quality and red as microbial safety this diagram would give a good explanation of high temperature short time processing). An example of this is the storage of dried mashed potato, at lipid oxidation dominates at low temperatures and Maillard browning dominates at high temperatures.



A second major problem is accounting for experimental error during the multiple curve-fitting steps in this procedure. Particularly in the Arhennius step, the natural log of the rate constant is calculated by fitting a straight line to the available data. There is clearly some error in this procedure and even a tiny error in ln(rate constant) can lead to a huge difference in rate constant, for example mis-calculating ln(rate constant) as –6.1 rather than –6.0 (~1.5% error) would lead to an almost 10% error in rate constant.

Rather than calculate the whole degradation curve it is sometimes preferable to assign a critical value for the measured parameter that is the minimum acceptable, the shelf life is the time taken for that parameter to deteriorate to the critical value under storage conditions.

Ted Labuza proposes a systematic series of steps to conduct *accelerated shelf life test* and (see section 17.3.6 in the Fennema text):

ASLT 1: Decide what are the acceptable limits for your product? Consider the nutritional and safety implications of spoilage first then the loss of quality. Most product qualities will degrade over time what are the limits your customers are willing to accept and which reaction is limiting?

ASLT 2: What kinds of reactions are likely to be important? Finding out a chemical mechanism for the degradation is important as it will give you insights into how to control it, how to measure it and possible harmful outcomes you have not considered.

ASLT 3: How will you pack the food? You should package your samples for shelf life testing in a similar way to the real food is stored (especially consider light exposure and humidity) bearing in mind that there may be limited space to store experimental samples.

ASLT 4: What storage temperatures should you use? This is a key question, Labuza makes some suggestions for different types of food but in each example consider that you will need enough heating to produce a change in reaction rate and not enough to fundamentally change the product or the reactions spoiling it.

ASLT 5: How long do you need to store at each temperature? You want your sample to change appreciably but you don't want to make unnecessary measurements.

ASLT 6: How will you test and how often? The analytical method chosen can be as specific as a chromatographic determination of an important compound or as general as a sensory score for the product. Remember to select an analytical method that corresponds as closely as possible to the limits set out in #1. Test as often as you can afford. Try to space out your testing so the amount of change in [parameter] between tests is constant rather than the amount of time before tests.

ASLT 7: Plot kinetic curves and calculate k and n. Find the best rate equation to fit your data.

ASLT 8: Plot log(k) against 1/T (i.e., Arrhenius) and calculate k at storage temperature.

ASLT 9: Plot the kinetic curve at the storage temperature and calculate shelf life. Use the same equation used in #7 and the rate constant calculated in #8. The limit of [parameter] is that set out in #1.

Reading exercise: Executive summary of the WHO report on the development of nutrition bars for refugee populations. What chemical issues must be overcome to develop a useful nutrition bar? Do you think it is advantageous to supplement the bar? How would you decide how much of a given vitamin to supplement the bar with?

Question 6: ASLT Testing. Use this data from an ASLT test to calculate the level of folic acid supplementation needed for a refugee bar to be a useful source of the vitamin after 30 months storage at 30°C. The vitamin content was measured as a function of time at four elevated temperatures. Assume vitamin degradation follows first order kinetics, calculate:

1. The rate constant at each elevated temperature
2. Plot an Arhennius curve and calculate the rate constant at 30°C
3. If one serving of the bar must contain the RDA of this vitamin after 30 months at 30°C, at what level must the bar be supplemented?

	Vitamin content normalized to initial value				
Time /months	at 80°C	at 100°C	at 120°C	at 140°C	at 160°C
0	1.020	1.000	1.000	1.000	1.000
0.5	0.985	0.933	0.821	0.637	0.361
1	0.974	0.874	0.652	0.375	0.136
1.5	0.949	0.812	0.557	0.258	0.028
2	0.914	0.749	0.447	0.167	-0.006
2.5	0.876	0.707	0.389	0.072	0.009
3	0.844	0.636	0.298	0.053	0.001
3.5	0.826	0.607	0.270	0.059	-0.023
4	0.835	0.569	0.225	0.019	-0.024
4.5	0.781	0.517	0.190	-0.001	-0.002
5	0.801	0.482	0.122	0.021	-0.021
5.5	0.772	0.461	0.098	-0.008	0.008
6	0.729	0.428	0.072	0.012	0.006

Do you recommend supplementation?