How to prepare pH 4 and 7 buffers from scratch without using a pH meter

I wrote [a post](#) in the past about how you could prepare pH buffers in order to calibrate your pH meter if you happen to already have a calibrated pH probe. This can generate decent results if the initial calibration of the probe is excellent and the sensitivity of the probe is high. This however might not be a possibility for some people – given that their pH probe might not be calibrated to start with – so in today's post I am going to tell you how you can prepare your own pH 4 and 7 buffers without having any other tools but a scale, distilled water and some raw salts. This tutorial will be made assuming you're preparing 500mL of each buffer but feel free to scale this up or down as you wish (these buffers are meant to give you a total 0.1M buffer concentration). *Note that pH depends on temperature, these buffers are meant to give pH values of 4 and 7 at 25C*.

To prepare these buffers you will need the following materials:

- [A scale that can weight with a precision of +/- 0.001g](#)

- Potassium citrate (food grade)
- Anhydrous Citric acid (food grade)
- Potassium monobasic phosphate (food grade)
- Potassium dibasic phosphate (food grade)
- Distilled water
- Two clean glass bottles to prepare and store the buffers. (I would recommend these, but any clean glass containers would do)

Follow these steps to prepare the pH 4 buffer:

1. Weight **exactly** 5.259g of potassium citrate and transfer that amount to the glass bottle
2. Weight **exactly** 6.309g of citric acid and transfer the solid to the same glass bottle
3. Fill the bottle to around 250mL using distilled water
4. Mix the solids using a glass rod or any other inert mixing utensil until fully dissolved
5. Fill the bottle to 500mL using distilled water.
6. Label the flask clearly so that you know this is the pH 4 buffer

Follow these steps to prepare the pH 7 buffer:

1. Weight **exactly** 3.369g of potassium dibasic phosphate and transfer that amount to the second glass bottle
2. Weight **exactly** 4.172g of potassium monobasic phosphate and transfer the solid to the same glass bottle
3. Fill the bottle to around 250mL using distilled water
4. Mix the solids using a glass rod or any other inert mixing utensil until fully dissolved
5. Fill the bottle to 500mL using distilled water.
6. Label the flask clearly so that you know this is the pH 7 buffer

The above should provide you with pH 4 and 7 buffer solutions that should be relatively precise. The exact volume of the solution is not critical, as the volume only has a strong effect on the buffering capacity but not on the final pH,

especially at relatively high buffering strengths. However, if you want to have more precision use 500mL volumetric flasks to prepare the solutions. The error in these buffers will depend on the purity of the salts used — which is why higher purity food grade salts are recommended above — as well as in the accuracy of the weighting and transferring processes. In order to obtain a higher accuracy you would need to purchase more expensive analytical grade salts and also use volumetric flasks to prepare the solutions, so that you can prepare them at the exact concentration intended.

Another limitation of the above buffers is that they do not contain any sort of preservative and they are both prepared with food grade substances that can attract fungi and bacteria. For this reason the above buffers will probably not last for a significant amount of time and should probably be discarded within a couple of weeks. However the chemicals used here are very cheap so — with the amounts purchased above — you should be able to prepare as much buffering solution as you might need. Note that the solutions can also be frozen in order to increase their shelf life, although keep in mind that since pH depends on temperature you will need to wait for them to reach room temperature before taking a reading.

It is also worth mentioning that these buffers will both be completely transparent, since they are prepared without any dies in order to give the maximum possible accuracy in the pH. However you can add a very small amount of food coloring to each one to provide a distinct color without causing a significant change in the pH, less than half a drop should be enough to give your solutions a distinct hue.

I would advice you do a pH check with a pH meter calibrated using a normal commercial solution the first time you prepare these solutions. This is just to be sure that you followed the procedure correctly and the resulting buffer is of the intended quality. Once you do this you should be able to create as much buffer as you desire without any problems.

Understanding the carbonic acid/bicarbonate buffer in hydroponics

I have written several articles before about pH and it's importance in hydroponic culture ([1](), [2](), [3](), [4]()). However I have yet to write a detailed explanation of one of the most important buffering systems in hydroponics, which is the carbonic acid/bicarbonate buffer. This buffer is significantly more complicated than the simpler buffer created using phosphoric acid species, as it not only relies on ions present in solution but also on the partial pressure of carbon dioxide in the atmosphere. In this article I will attempt to explain this buffering system in detail, shining some light into the limitations of this buffer and how changing different key variables can fundamentally affect the way it works in hydroponics.
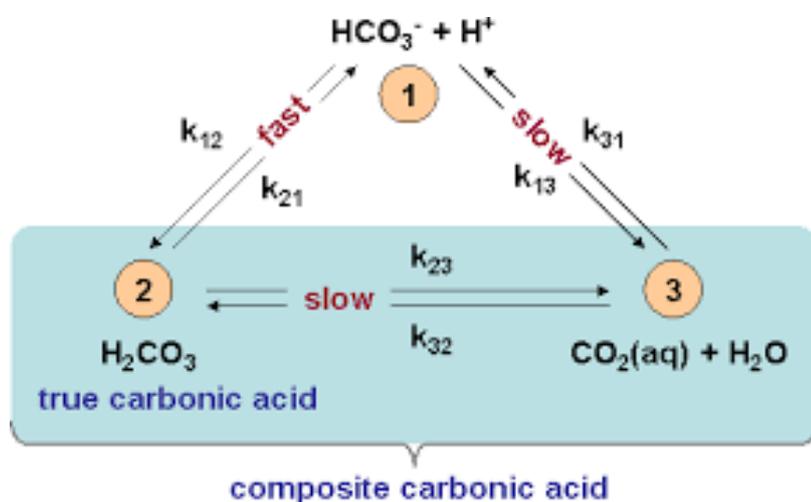
Chemical reactions involved in the carbonic acid/bicarbonate buffer. Taken from [here]().

A buffer is nothing more than a pair of chemical species in solution that are present at a certain pH, that can react with additional H_3O+ or OH- ions that are introduced into the solution. Since these ions control the value of pH, anything that prevents their concentration from changing will keep the pH stable. Distilled water, for example, has absolutely no buffering capacity since within it there is nothing that can react with incoming H_3O^+ or OH^- ions that are added to the solution. Distilled water should therefore have a pH of 7.0, it does not because we live in an environment where an acid can always be generated from the air. This acid — carbonic acid — is generated in water whenever it's put into contact with a carbon dioxide containing atmosphere. *This makes distilled water have a pH of around 5.6*.

To be able to calculate the pH we need to consider all the chemical equilibrium reactions that happen, these are summarized here and in the image above. We must consider that carbon dioxide will dissolve in water to always satisfy Henry's law, that dissolved carbon dioxide will be in equilibrium with carbonic acid, that carbonic acid can dissociate into a H_3O^+ ion and a bicarbonate ion and that a bicarbonate ion can further dissociate into an additional H_3O+ ion and a carbonate ion. To solve all of this we must also consider that charge neutrality must be preserved, meaning that the sum of all molar charges of all positive ions must be equal to the molar charges of all negative ions. To carry out these calculations I routinely use the freely available Maxima software. Below you can see the code I use to solve this system in Maxima (constants are taken from here):

```
[kw : 10^(-14.0), kh: 1.7*10^(-3.0), kc1: 2.5*10^(-4.0), kc2:
4.69*10^(-11.0), co2: 1.32*10^-5];
log10(x) := log(x)/log(10) ;
pH(x) := float(-log10(x));
```

```
float(solve([h*oh=kw, h = 2*co3+hco3+oh, kh=h2co3/co2,
kc1=(hco3*h)/h2co3, kc2=(co3*h)/hco3],[oh, co3, hco3, h2co3,
h]));
```

This is the solution obtained for the molar concentrations
(rounded for clarity):

```
oh    = 4.21*10^-9
co3   = 4.68*10^-11
hco3  = 2.36*10^-6
h2co3 = 2.24*10^-8
h     = 2.37*10^-6
```

After executing this code you will get several different
possible solutions, but the only one that interests us is the
one where the H_3O^+ (h) concentration is a positive number (this
solution is showed above). We can then use the pH function to
calculate the value of pH for this H_3O+ concentration, which
gives us a value of 5.62, this matches the real measurement of
a distilled water solution at 25C under a 387ppm carbon
dioxide atmosphere. Note that the amount of none dissociated
acid in solution is very small. Taken to mass, the
concentration of carbonic acid is 0.00138 ppm. However the
concentration of bicarbonate is significantly greater, at 3.6
times the concentration of undissociated carbonic acid. This
explains why the pH drops so much, since a significant amount
of the generated carbonic acid ends up dissociating and
contributing H_3O^+ ions to the solution. This also shows you how
little acid is needed to drop the pH of an unbuffered
solution.

To create the buffer with the biggest possible strength we
would need to add enough strong base to shift the pH to the
point where the pH equals the pKa (which is just -
Log(equilibrium constant)) of the joint reactions created from
the reaction of carbon dioxide with water to create carbonic
acid and the subsequent dissociation of this acid into

bicarbonate and H_3O^+. This point is at 6.3 under atmospheric conditions at 25C. This can be achieved with the code below:

```
[kw : 10^(-14.0), kh: 1.7*10^(-3.0), kc1: 2.5*10^(-4.0), kc2:
4.69 10^(-11.0), co2: 1.32*10^-5, h:10^(-6.3)];
float(solve([h oh=kw,  base+h = 2co3+hco3+oh, kh=h2co3/co2,
kc1=(hco3 h)/h2co3,  kc2=(co3 h)/hco3],[oh,  co3,  hco3,
h2co3,base]));
```

This is the solution obtained for the molar concentrations(rounded for clarity):

```
oh    = 1.99*10^-8
co3   = 1.04*10^-9
hco3  = 1.11*10^-5
h2co3 = 2.24*10^-8
base  = 1.07*10^-5
```

The pH here is set to 6.3 and we can see that to get there we would need to add a base at a concentration of $1.07*10^{-5.0}$. If this base was KOH this would imply adding it at a rate of 0.6 ppm. We can see how the pH changes as a function of adding base or acid from this point. If at this point we decided to double the addition of strong base we would get to 6.57, tripling it would take us to 6.73 and adding 10 times more base would take us to 7.25. The buffer is indeed resisting the increase in pH by basically drawing CO_2 from the air to react with the incoming base as base is added to the solution. *However you might notice that under equilibrium conditions the buffering capacity of this system is very low*. Just 6 ppm of a KOH equivalent strong base addition can strongly affect the pH — taking it from 5.6 to 7.25 — so how can the carbonic acid/bicarbonate buffer be effective at all in hydroponics?

The answer is in the first image in this post. The equilibrium reaction between carbonic acid and water plus carbon dioxide in water (k23/k32) is fundamentally slow. We can take advantage of this by generating larger amounts of carbonate species in solution through the use of exogenous carbonate or

bicarbonate additions and then setting the pH at a lower value to generate more carbonic acid, this acid will then take some significant time to reach equilibrium. This is the reason why using tap water with a significantly high alkalinity can provide a surprisingly stronger buffer than what would be expected at equilibrium and it also has some interesting consequences in the use of nutrient solutions.

Let's consider a case where there is no decomposition of carbonic acid — let's suppose it's extremely slow — and say we add 100 ppm of potassium carbonate into a solution and then set the pH back to 5.8 using phosphoric acid. In this case the predominant reactions in solution would be the dissociation of dihydrogen phosphate to hydrogen phosphate and H_3O+ and the carbonic acid dissociation discussed before. In order to properly consider this case we must also introduce two additional equations, mainly the mass balance equations for the phosphate and carbonate species, since this time we are assuming no carbon dioxide is ever lost to the atmosphere. Note that I have changed the equilibrium constant for the carbonic acid reaction here to $10^{-6.3}$ where carbonic acid is now "apparent carbonic acid". You can see the equation system and solution below:

[kw : 10^(-14.0), kh: 1.7*10^(-3.0), kc1: 10^-6.3, co2: 1.32*10^-5, kp:10^-7.2, total_p: 1.7*$7.23$10^-4, total_c: 7.23*10^-4];

float(solve([h*$oh=kw$, total_c=hco3+h2co3, total_p=h2po4+hpo4, 2*total_c+h = hco3+oh+h2po4+2*$hpo4$, kc1=(h*$co3$h)/h2co3, kp=(hpo4*h)/h2po4],[hco3, h2co3, h2po4, hpo4, h, oh]));

This is the solution obtained for the molar concentrations(rounded for clarity):

hco3   = 1.72*10^-4
h2co3 = 5.50*10^-4
h2po4 = 0.00118
hpo4   = 4.64*10^-5

$h \qquad = 1.60*10^\wedge-6$

The final pH of this solution is very close to 5.8 and the concentration of P is 47.9 ppm with K at 38.10 ppm. Notice however that apparent carbonic acid has a concentration of $5.50*10^{-4}$ M, which implies that the system is not at equilibrium since this amount is significantly larger than what we would expect from Henry's law. If we reduce the concentration of carbonic acid to half then the pH will increase to 6.01, as we would expect from extracting an acid from the solution. The implication is that — with time — the pH of this solution is going to slowly increase, as carbonic acid decomposes and the solution reaches an equilibrium with the atmospheric carbon dioxide level. This is also why nutrient solutions that are prepared with tap water high in carbonates and then aerated will tend to show a rapid increase in pH — even if the solution is not fed to plants — as the reaching of equilibrium is accelerated by the agitation of the solution and the contact with air (that allows CO_2 in solution to escape).

As soon as the above solution is prepared it offers a substantially superior buffering capacity when compared with a solution containing only phosphates. This is why water with high alkalinity tends to provide better pH stability in drain to waste type systems when compared with solutions prepared with RO water. This water contains a significant amount of carbonates that are turned into carbonic acid and bicarbonate as soon as the pH is lowered to the pH range used in hydroponics. As long as the solution is used quicker than the carbonic acid decomposes, there will be a substantial increase in pH stability.

If you are using RO water or water with low alkalinity to prepare your solutions you can obtain a similar effect by adding 100-200 ppm of potassium carbonate before you start preparing the nutrient solution, you can similarly use

bicarbonate but I would recommend using potassium carbonate, as it is cheaper. It would also be advisable to use the solution as fast as possible, since time will cause the solution to reach equilibrium and the pH to increase. This effect will take much longer if the CO_2 concentration is higher — which is true for setups that use enriched CO_2 — or if the temperature is lower, which increases the solubility of CO_2.

A guide to different pH down options in hydroponics

The control of pH in hydroponic nutrient solutions is important. Plants will tend to increase the pH of solutions in most cases — as nitrate uptake tends to dominate over the uptake of other ions — so most growers will tend to use pH down much more than they use pH up. While most growers prefer to use concentrated strong acids, there are a wide variety of different choices available that can achieve different outcomes at different cost levels. In this post I want to talk about different pH down options in hydroponics, along with some of their advantages and disadvantages.

Hydrangeas change color as a response to different pH values in soil

The first group of pH down chemicals are strong acids. These are technically acids with very low pKa values, meaning they react instantly with water to generate at least one mole of hydronium for each mole of added acid. They offer the strongest ability to drop pH per unit of volume, which makes them more cost effective. However the fact that they often need to be diluted to make the pH addition process practical — because of how much the concentrated forms can change pH — can make their use more difficult than other forms of pH down. These are the most common options:

Phosphoric acid (from 20 to 85% pure): This acid doubles as a plant nutrient, meaning plants will be affected by the phosphorus added. It is commonly used in food — so food grade phosphoric acid can be bought cheaply — it also has additional deprotonations with strong buffering at a pH value of 7.2 with buffering capacity against bases getting stronger as the pH goes down all the way to 6.2. This is the most commonly used acid by hydroponic growers.

Sulfuric acid (from 20 to 98% pure): This acid is commonly used in car batteries and offers the largest pH dropping ability per unit of volume among all the strong acids. It is however important to use food grade sulfuric acid in hydroponics as normal battery acid can include some metallic impurities — from the fabrication process of sulfuric acid — that might negatively affect a hydroponic crop. Food grade sulfuric acid is safe to use in hydroponics. A big advantage is that plants are quite insensitive to sulfate ions — the nutrient provided by sulfuric acid — so adding sulfuric acid does not really affect the nutrient profile being fed to the plants. Note however that most battery acid products in developed countries are also ok, as the quality of these acids demands the metallic impurities (more commonly iron) to be quite low. If in doubt, you can do a lab test of the sulfuric

acid to see if any impurities are present.

Nitric acid (from 30-72% pure): This acid also provides nitrate ions to plants, so it also contributes to a solution's nutrient profile. It is however more expensive than both phosphoric and sulfuric acids and more heavily regulated due to its potential use in the fabrication of explosives. The acid itself is also a strong oxidant, so storage and spillage problems are significantly worse than with phosphoric and sulfuric acid. Although this acid can be used in hydroponics, it is generally not used by most growers due to the above issues.
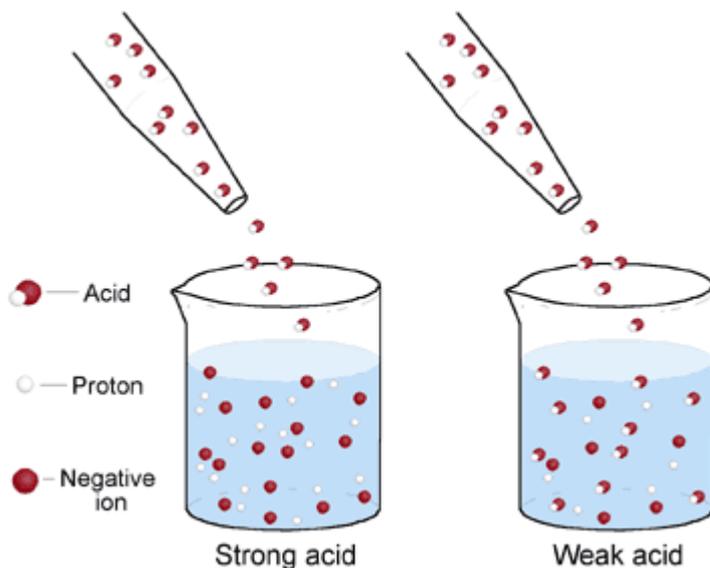

Diagram showing the dissociation of a strong vs a weak acid

The second group of pH down chemicals are weak acids. These are acids that do not generate at least one mole of hydronium ions per mole of acid when put in solution, but do provide a pH down effect as some hydronium ions are generated. This means that larger additions will be needed to cause the same effect but at the same time their handling is usually much safer than for strong acids. Here are some options that could be used as a pH down.

Common food grade organic acids (citric acid, acetic acid, etc): Organic acids are a very low cost way to lower the pH of a hydroponic solution as many of these are available off the shelf in super markets in food grade qualities. The main issue

with organic acids — which anyone who has used them has probably experimented — is that the effect of the acids does not seem to hold (pH goes up quickly after the acid is added and the solution comes into contact with plants). This is actually caused by the fact that plants and microbes can actually use the conjugated bases of these ions nutritionally, causing an increase in pH when they do so. The initial addition of say, citric acid, will drop the pH — generating citrate ions in the process — these will then be absorbed by microbes and plants, increasing the pH again rapidly. *The use of these acids is therefore not recommended in hydroponics*.

Monopotassium phosphate (MKP): This salt contains the first conjugate base of phosphoric acid and is therefore way less acidic than it's full on acid partner. Since it's a solid its addition is way easier to control compared to the acid and it can also be handled safely with minimal precautions. It provides both potassium and phosphorous to a solution — both important nutrients — and therefore needs to be used carefully when used as a pH down agent (as it significantly affects the nutrient profile of the solution). Since it adds both a cation that helps counter pH increases by plants and phosphate species it provides a double buffering effect against future pH increases. It is a very common ingredients of commercial pH down solutions for this reason.

Monoammonium phosphate (MAP): Similar to the above, except for the fact that this salt adds nitrogen as ammonium, which is a nitrogen form plants are very sensitive to. Plants will uptake ammonium preferentially over any other cation, so MAP provides a very strong buffering effect against nitrate absorption, with potential problems if too much is used (although this depends on the plant species being grown). When MAP is used as a pH down its addition therefore needs to be carefully controlled in order to avoid excess usage. Due to the presence of this powerful ammonium buffer, MAP is generally very effective at preventing future increases in pH, although this

might be at the expense of yields or quality depending on the crop.

Potassium bisulfate: This salt contains the first conjugate base of sulfuric acid and is therefore a powerful tool to decrease the pH of a solution. The resulting sulfate ions provide no chemical buffering effect, so the only buffering effect in terms of plant absorption comes from the addition of potassium ions, which can help mitigate nitrate absorption. This salt is also considerably expensive compared with the two above — which are commonly used fertilizers — and is therefore seldom used in hydroponics.

Which is the best pH down solution? It depends on the characteristics of the growing system. Generally a pH down solution needs to be easy to administer, cheap and provide some increase in buffering capacity overtime — to make additions less frequent — so the pH down product or combination of products that best fits this bill will depend on which of the above characteristics is more important for each particular user.

People who use drain-to-waste systems usually go for stronger acids, since they only adjust pH once before watering and then forget about the solution. This means that additional buffering capacity in the solution is probably not going to be very important and cost is likely the most important driving factor. If injectors are used then the strong acids are often diluted to the concentration that makes the most sense for them and most commonly either phosphoric or sulfuric acids are used.

For growers in recirculating systems options that adjust pH with some added buffering capacity are often preferred, because the same solution is constantly subjected to interactions with the plants. In this case it's usually preferred to create a mixture of strong and weak buffering agents so that both quick decreases in pH and some increased

protection from further increases can be given to the solution. In automated control systems using something like a concentrated MKP solution is preferable over any sort of solution containing phosphoric acid, as issues from control failures are less likely to be catastrophic.

Preparing your own buffer solutions for pH calibration

If you are interested in learning how to prepare buffers without needing a previously calibrated pH probe, please read [this post](#).

One of the most common tasks that hydroponics growers have to carry out is to calibrate their pH meters in order to ensure that the readings are accurate. To do this it is generally necessary to buy somewhat expensive pH buffer solutions that will only last for a relatively small while before new solutions have to be bought. However the fact of the matter is that you don't need to buy these solutions forever and you can actually make your own using a few chemicals. This will be a ton cheaper than buying buffer solutions and will allow you to prepare solutions whenever you need them.

To calibrate a pH meter for hydroponics we generally need two different buffer solutions. One of these solutions needs to have a pH of 4 and another one needs to have a pH of 7. You can actually calculate the exact amount of chemicals you need to add to create these buffer solutions but this assumes that your water source is very pure (distilled water) and that your chemicals are also very pure and standardized. To make

buffer solutions in less-than-ideal conditions we need to have a calibrated pH meter, which means you will need to purchase some buffer solutions, but only once.

After you have calibrated your pH meter ensure that the pH meter measures the exact value that you want to prepare within the buffer solution you have purchased. So make sure that the pH meter when placed in the pH 7 buffer solution measures 7 if this the solution you want to prepare and make sure it measures 4 when placed in the pH 4 buffer solution if this is what you want to make. Once you have the pH meter in a coherent state with the solution you want to prepare we can now proceed to make a new buffer solution.

To do this first fill a contained with tap water, make sure you don't fill it to more than 80% of its volume (to account for some volume expansion when we add the solids) and use your calibrated pH meter to measure its pH. For the pH 7 buffer add 10g of mono potassium phosphate per liter of solution (this doesn't need to be exact) and stir the solution until it dissolves. Then add KOH slowly, add it flake by flake, while you measure the pH until your pH reaches 7.00. You will notice that as the pH approaches 7 you will need more KOH to change the pH. If you go a bit above the intended pH you can add mono potassium phosphate to decrease it to 7.00. For the pH 4 solution you can perform the same procedure but instead add 20g per liter of citric acid and then add KOH slowly to increase the pH up to 4.00. After preparation leave the buffers to rest for a few hours and measure the pH again to ensure that your solution pH remains stable. Remember to store any prepared buffers in air-tight bottles and store these bottles in dark places.

What we are doing with the above procedure is basically adding two acidic substances which have pKa values close the pH values that interest us. Close to 7 (mono basic phosphate) and

close to 4 (citric acid). We then generate the necessary amount of conjugate base to reach the necessary pH level by adding KOH. The buffer strength is established by the initial amount of the acidic substance we add and the role of the KOH is basically to move the buffer pH to the point where we want it, a point that has a very high buffer capacity given the pKa values of the acids used.

Of course the above is very far form the ideal analytical procedure to prepare a buffer but it's the easiest, cheapest and most effective way to prepare a buffer that is accurate enough for pH meter calibration use in hydroponics at a minimum cost. Sure, it requires an initial pH calibration — which can be a bit inconvenient — but you can buy a small couple of buffer bottles to calibrate and then prepare 2 gallons worth of pH buffer that you can then use to calibrate your pH meters for a long time. If you use tap water to prepare the above and some solids precipitate you can filter them before storing your solutions. Then measure the pH again after filtering to ensure that everything remains stable.