



Buffers, the Acid Rain Slayer: Crash Course Chemistry #31

Crash Course: Chemistry

<https://youtube.com/watch?v=8Fdt5WnYn1k>

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=====Nature is Nutty (00:00)=====

Hank Green: A few months ago, when we first talked about acid base reactions, we saw how acid rain could melt the face off a statue. Which is better than melting your face off, which some acids can do. So consider yourself lucky.

Acid rain forms when sulfur dioxide emitted from burning fossil fuels reacts with water in the air to form sulfuric acid. And back when acid rain was at it's worse, in the 80s and 90s, it was the scourge of pristine waterways all over Europe and North America. Some rivers and streams were left completely devoid of algae and fish. In Montana, where I live, we saw quite a bit of acid rain too, as that statue can attest, but oddly enough rivers and streams here did not suffer the same horrible effects as other places.

=====Carbonate Buffering and Acid Rain (00:35)=====

This, that I'm standing in right now, is the Clark Fork River. It remains relatively unharmed by acid rain. In fact, when the water that fed it had a pH of 4.5, the river remained basic. This is a dropper full of dilute sulfuric acid, think of it as a model for acid rain. And this is just distilled water with a pH indicator in it that makes it blue when it's neutral or basic and it'll turn pink if it's at least a little bit acidic.

Let's see how much acid it takes to turn our distilled water a little bit acidic. Let's do one drop. Oh wow! It's already pink guys, it's already pink. One drop. Let's try the same thing with the river water. Let's see how many drops it takes before it turns - I'm just - it's just - I'm just dumping it in there. We getting it? It's starting to happen now? There, it's sorta half and half. We've got a half and half transition. After, after like five, or six, or seven drops. That was a lot more. And we're not even all the way there. Get, get a little bit more, a little bit more, a little bit more, c'mon. There we go! There, there now it's acidic.

Why does this happen? It's because this river is protected by limestone. Which is calcium carbonate that is present throughout the entire river system. Acid rain dissolves the calcium carbonate in the limestone, that carbonate washes in to the river and acts as a natural buffer.

=====Composition of Buffers (01:47)=====

A buffer solution resists changes to it's pH when a strong acid or base is added to it. So the Clark Fork geochemistry explains why acid rain isn't as devastating here as it is in say the Adirondack Mountains of New York where there is no limestone.

Buffering is a big deal in chemistry. We buffer swimming pools to prevent the chemicals from damaging our skin, and we buffered soda pop to prevent the acidic flavorings from damaging our teeth and tissues. We even have buffers in our blood to keep our internal pH constant and ourselves healthy.

I think it's important to learn about something that powerful. How about you?

[CrashCourse intro]

=====Definition of Buffers (02:26)=====

A buffer solution is a mixture of a weak acid plus its conjugate base, or a weak base plus it's conjugate acid. These are called acid-base pairs. Weak in reference to acids and bases means that they only partial dissociate. It's actual their weakness that makes them great buffers. Since they don't fully dissociate in water, the undissociated buffer can act as either a source or a sink for protons. Which helps neutralize a strong acid, or base, that's added to the solution.

It's really all about equilibrium. For example, when weak acid like acetic acid is added to water, a tiny fraction of it dissociates in to its constituent ions: acetate and hydrogen ions, or protons. I was recently pouring a bunch of a solution like this all over my fish and chips. Vinegar is just a 5% solution of acetic acid.

But the reaction is reversible as well, and that's where equilibrium comes in. Say we have a 1 molar solution of acetic acid, to make the solution a buffer we need to increase the concentration of acetic acids conjugate base, acetate, by adding sodium acetate to it. That would be a good way. Sodium acetate dissociates completely, thereby providing a ton of acetate ion.

=====pH of Buffers (03:29)=====

To see how this works in practice, let's add enough of that salt to make a 1 molar solution. We know how much acid and how acetate we put in, but the important thing is the pH. And to determine that, we have to know how many protons there are.

A Rice table will help us keep track of everything! The reaction, R, we're interested in here of course, is the dissociation of acetic acid. We can ignore the sodium from the sodium acetate, although it will stick around, it's just a spectator ion that won't take part of any reactions.

Our solution contains initial concentrations I of 1 molar acid and 1 molar acetate. We haven't formed any hydrogen ions yet, so that stays at zero for now. We don't know how much the concentrations will change, C, so we call it 'x'. The acid loses 'x' and both ions gain 'x'. So our at equilibrium, E, then are 1 minus x, 1 plus x, and simply x - in that order.

Now just put the numbers in to the equilibrium formula, 1.76×10^{-5} . But when chemists work with dissociation equations, for acids and bases, they give the K_{eq} a special name: the acid (or base) dissociation constant. The symbol for this kind of equilibrium constant is K_a , for an acid, or K_b for a base.

So use the equilibrium expression for acetic acid, and put in the K_a , and the equilibrium concentrations from the RICE table. With a little simple algebra, it simplifies - simplifies? That doesn't, that doesn't look simplified. I guess you could call that simplifying, but ugh...that's like quadratic, I don't want to do that. So here's a little trick to make this a lot easier.

See acetic acid is a really weak acid. So only a tiny fraction of it dissociates. Which means that 'x' is super small. If it's so small that after rounding for significant digits it doesn't change our answers at all, then why not just drop it? Then that first x for the hydrogen ion has more effect because it's multiplied, but the other two? Let's just forget they're there and see what happens.

If we go back to where we plug in all the numbers and simply drop the two 'x's that are being added and subtracted, the rest of the problem cancels out leaving x to equal 1.76×10^{-5} . The rest is a breeze with a couple taps of the calculator we find that the pH is 4.754.



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But here's the big question, what if we tried to push the pH out of whack? The whole point of a buffer is to resist that, right? If I add a strong acid, like say hydrochloric acid, at a concentration of like 0.1 mole per liter to distilled water. The pH will change, very quickly. To like, very fast, dropping, yes. Now we're at like a 3, pH of 3. Not a healthy environment for most organisms.

So let's think about what would happen to the pH with a buffer in place. Even though HCl dissociates completely in water, releasing tons of hydrogen ions, when it's added to a solution that's buffered with acetate, the excess hydrogen ions join with the acetate ions to form acetic acid. Thus that strong acid can't effect the pH much because the hydrogen ions are used up.

To neutralize .01 molar HCl, or more specifically .01 molar H^+ , the acetate concentration much decrease by 0.01 moles per liter. Simultaneously increasing the acetic acid concentration by 0.01 moles per liter. That leaves us with .99 molar acetate and 1.01 molar acetic acid. Well pH is determined from the concentration of protons, which is in our equilibrium equation so let's just solve for that.

When you plug in the new acetic acid and acetate concentrations and the K_a , you get 1.80×10^{-5} moles per liter for the proton concentration. Which translates to a pH of 4.746.

This is obviously not a big change from 4.754. In fact I had to go out to the fourth digit to see the pH change. Which isn't even justified if you watch CrashCourse Chemistry on significant figures. But I have to confess vinegar and hydrochloric acid they may make things easier to understand, but they're not exactly super relevant in terms of practical chemistry.

=====Carbonate Buffering in Nature (07:12)=====

Instead I want you to see how this works in the 'real' real world. So, let's consider the buffering system of the Clark Fork river. There the reaction between dissolved limestone and acid rain really happens in three steps.

First, the solid calcium carbonate reacts with the protons from acidic rain to form calcium and bicarbonate ions. The bicarbonate ions each have one hydrogen. As long as protons are available, the bicarbonate ions can grab a second proton to become uncharged carbonic acid. As you can see this chain reaction uses up two protons per molecule of calcium carbonate. That makes this process doubly powerful. And that explains why the Clark Fork river is so resistant to acidification.

=====Titration (07:43)=====

But of course buffers are not invincible. Add enough acid or base and even the best buffered solution will get overwhelmed. We call that threshold the buffering capacity of the solution. And we determine it in the lab using pH indicators through a process called titration.

Earlier I used a pH indicator that showed an acidic pH by turning pink. But there are lots of other indicators, each with different colors and a different pH where it changes. This is called the indicators end point.

Here we have 100 mL of water from the river to which I've added some pH indicator. It's actually a mix of two different pH indicators: bromocresol green and methyl red. That work together well for this

reaction. It'll stay blueish in color for as long as the bicarbonate ions are around to keep the pH buffered above the indicators end point of pH 4.

This long glass thing here is a burette. It's for dispensing liquids in a very controlled way, while also keeping track of how much you've dispensed. At the moment it contains exactly 25 mL of a 0.10 molar sulfuric acid solution. The thing to do is to add the acid very slowly, stirring as I go, which is being done for me by this automatic stirrer thing which is quite nice. And - and - you can do it a few ways. If you have a guess at how much you can put in, you can just sorta turn it on and let it go, but I don't know so I'm just gonna let it drip. Very slowly. You can turn it very slightly and you can actually get it to do sorta drippy drips. So then you're like, waiting to see if there's some changing happening. And there's a little bit of changing happening, but now it's going back. So, we're getting closer. And what I'm doing right now, is I'm actually adding less than a drop at a time by going quickly past the opening in this little burette thing.

I can actually see the reaction happening, right before my eyes. It's beautiful, and then it goes back. It's right now a paler blue than it was before which is exciting. It means we're getting close! This is the stuff I get excited about. I know I'm a nerd. Ohhh, it's almost white right now, it's like a pinkish, purpley. Ohhh, beautiful! That was perfect!

The solution is now staying pink which means that I've exhausted it's buffering capacity, and the pH has dropped below the indicators end point. The volume in the pipette is now 22.4 mL, meaning that I used 2.6 mL or 0.0026 liter of the acid solution. The acid solution is 0.1 molar. So multiplying these numbers together tells me that I used 0.00026 mole of H_2SO_4 .

Sulfuric acid reacts at a one to one ratio with calcium carbonate, so assuming the calcium carbonate is the only buffer in the water, the 100 mL of river water here must also contain 0.00026 moles of calcium carbonate. Making it a 0.0026 molar or 2.6 mM solution.

I'm a big fan of protecting the environment, but sometimes it is amazing to see what nature can do to protect itself. We live in an amazing world and I wouldn't trade it for anything. Not even Mars.

=====Summary & Credits (10:50)=====

Thanks for watching this course of CrashCourse Chemistry. If you were listening, you learned that some bodies of water, like the Clark Ford river, have natural protection from acid rain in the form of a buffering system. You learned that a buffer is a solution that resists changes in pH. You learned how to make a buffered solution. And you learned how to calculate the pH of such a solution by various methods, including titration. And lastly, you learned the importance of the carbonate buffering solution in nature.

This episode was written by Kim Krieger and Edi González. It was edited by Blake de Pastino. And the chemistry consultant was Dr. Heiko Langner. It was filmed, edited, and directed by Nicholas Jenkins. Our script supervisor and sound designer was Michael Aranda and our graphics team was ThoughtCafé.