

Chemistry: Challenges and Solutions
Unit 6: Quantifying Chemical Reactions
Stoichiometry and Moles
Hosted by David Song

[Tease]

There are over 200 billion stars in our galaxy. But the number of molecules in this single drop of water is about ten billion times larger.

When dealing with such large numbers, how does a chemist even begin to precisely measure the ingredients in a chemical reaction? To quantify chemical reactions chemists use stoichiometry. Balancing equations, calculating molecular masses, and figuring out which ingredients will run out first, are all important tools in the science of stoichiometry.

CHARLISS DENNISTON: You need to know exactly how much of your reactants to add together to create your desired product otherwise there will be a lot of waste, you may not get chemical reactions to go fully to completion, so that's really valuable for us.

Using stoichiometry to quantify chemical reactions is essential in any problem you are trying to tackle from creating renewable energy sources to developing chemicals made from sustainable materials.

DANIEL NOCERA: Every single thing happening in life is a chemical reaction, so you better know how to quantify chemical reactions.

[Title: Unit 6 Quantifying Chemical Reactions]

DAVID SONG: This is just an ordinary gallon of water. But what if I told you that this gallon of water could provide enough energy to power a house for an entire day?

Hi, I'm David Song of the Nocera Laboratory at Harvard University. We're working on understanding how to create cheap, clean, and renewable energy. And this water is part of the solution, as we take on an impending energy crisis.

[SEGMENT 1: A Balanced Equation for Fuel]

In 2010, the world's total primary energy consumption was about 500 quadrillion BTUs. And that number is expected to almost double by 2050.

DANIEL NOCERA: Energy's going to double, double from what we use today. So it's a lot of energy. So we better figure out a new energy source, and you know what I want to use? The sun. Here's my future. All you need is sunlight and a puddle of water on the ground, and you are good to go with energy.

At the Nocera Lab at Harvard University, scientists are striving to create a sustainable energy supply through research in chemistry and biology.

Nocera and his team have created a prototype of a device that will convert the sun's energy into chemical energy: energy that has the potential to power a house or a car. Designed to mimic photosynthesis, they call it the artificial leaf.

In photosynthesis, plants absorb water from the soil and then use energy from the sun to rearrange the bonds of water. The hydrogen from the water combines with carbon dioxide to make sugar, and the oxygen in the water is turned into oxygen gas and is released back into the atmosphere.

Nocera's artificial leaf simplifies this process and uses the sun's energy to rearrange the bonds of water into hydrogen and oxygen.

DANIEL NOCERA: So that's what we're trying to do – is make things that mimic that photosynthetic process of water rearrangement to hydrogen and oxygen.

To separate the oxygen and hydrogen, the artificial leaf's silicon wafer is coated on each side with a catalyst. One side contains cobalt and promotes the separation of oxygen, and the other side contains nickel and promotes the separation of hydrogen.

In the lab, the artificial leaf is placed in a solution of water, and instead of the sun, a light is added.

DAVID SONG: So as the light source is hitting the artificial leaf, it is absorbing that energy to rearrange the bonds of water, H_2O , into oxygen on one side and hydrogen on the other side.

DILEK DOGUTAN KIPER: So, once you split water to hydrogen and oxygen, you have the opportunity to store them separately, and then use them as fuels. So, that's the goal here, splitting water and then making new energy sources.

CHRISTOPHER GAGLIARDI: There's a lot of different ways that you can get energy from hydrogen. One of them is to feed it into a fuel cell. This is actually what's running hydrogen cars right now.

Fuel cells take in hydrogen and oxygen and create electricity and the only by-product is water.

DANIEL NOCERA: Hydrogen is a really powerful fuel. So one thing you could do is use the hydrogen in a fuel cell. But, it would be better if I could have hydrogen get converted into a fuel that we use, like gasoline. Making liquid fuel would be a really good thing for the artificial leaf.

To figure out how to create a liquid fuel from the hydrogen gas, the researchers turn to biology.

CHRISTOPHER GAGLIARDI: The chemical problem of taking a gas and turning it into a liquid fuel is quite challenging, but it so happens that biology does this as an everyday occurrence. And so what we want to do is take the hydrogen and the oxygen that's created and try and feed it to an organism that is able to convert that into a usable liquid fuel.

The organism that the team is hoping to use to produce liquid fuel is called *Ralstonia eutropha*, a bacteria found in both soil and water.

JOSEPH TORELLA: Here we have *Ralstonia eutropha*. They're a simple organism that can convert hydrogen, oxygen, and carbon dioxide into both more cells in order to grow, and with a little bit of genetic tinkering, into biofuels.

To determine the amount of hydrogen that can be produced from a given amount of water, we must start with a balanced chemical equation. Each side of the reaction must have the same amount of each type of atom.

DAVID SONG: So to balance our equation we start with water, H_2O , which we can write here as H-O-H. This is just one way to write out one molecule of water. Now, we'll split our water molecule into its parts: hydrogen and oxygen. So the other side of the equation will look like this: two hydrogen atoms, plus one oxygen atom. However, in nature oxygen and hydrogen don't exist as individual atoms but rather as diatomic molecules. So, we can add a bond to these hydrogen atoms, and then we need to add an extra oxygen atom. But now we have one, two, three atoms on the left side, and one, two, three, four atoms on the right side, making this an unbalanced equation.

Each side of the equation has to have the same number of each type of atom. So what we can do is add a molecule of water on the left, and what that does is balances the number of oxygens on each side. Two on this side, and two on this side. But now our hydrogens aren't balanced. There are four on the left side and only two on the right side. But if we add another molecule of hydrogen on the right, then our hydrogens are balanced with four on each side and our entire equation is balanced with six atoms on each side. In shorthand, we write this as two H_2O yields two H_2 plus O_2 .

Now we know two molecules of water are going to generate two molecules of hydrogen gas and one molecule of oxygen gas. And with this equation, we can determine how much hydrogen we can produce with a given amount of water.

DANIEL NOCERA: You need to quantify chemical reactions because every single thing happening in life is a chemical reaction, so you better know how to balance those equations.

Through a series of equations, the team has calculated that by using the artificial leaf technology, the amount of water needed to power an average American household for a day is about two gallons, while someone living in a developing country would need about three cups of water for their average daily energy consumption.

DANIEL NOCERA: So imagine if you made your hydrogen at your house, you don't need to get electricity from anybody, you don't need to get gasoline from anybody. Your house is your own energy. All you need is some sunlight, water, and an artificial leaf.

[SEGMENT 2: DEMO – Making Water 2:1]

DAVID SONG: To make water we need two parts of hydrogen and one part oxygen. But how can we show this two to one ratio in the lab?

WOLFGANG RUECKNER: We're going to see what happens when we combine hydrogen and oxygen in this little piece of apparatus, it's just a little fish tank with a glass tube. What we'll do is combine equal parts of oxygen and hydrogen. They're not going to combine by themselves because there's not enough energy present to make them combine. So we're going to put in some energy by using a high-voltage spark. I'll turn that on. That's 2,500 volts, that's not something you want to play with at home.

So let's begin. We've got hydrogen here. I'll put on my safety glasses. And first fill this little tube with water, invert it, and then bubble some hydrogen gas into the tube until it's full. I'll transfer it into the big tube, and the bubbles go up to the top, so there you have it, there's one part of the hydrogen. Now I'll repeat that, and add another small test tube full. So now we have two parts hydrogen. Next we'll add two parts of oxygen. There's one part and another part. Ok, so we've got two parts oxygen, two parts hydrogen. They're mixing together and next I'm going to put the wire, where you saw the spark, into the tube. So that the spark is going to happen where the gases are mixed.

A small amount of water was created, which joined the rest of the water in the test tube, but some gas is left over. What's left over is the oxygen because water's not H_2O_2 – it is H_2O . So we have two parts hydrogen and one part oxygen to make the water. And we have left over one part of oxygen.

[SEGMENT 3: Calculating Molar Mass]

DAVID SONG: This one liter bottle holds about 26 sextillion molecules of air. Chemists measure things in big numbers. Our useful tool to make this more manageable is a unit of measurement called the mole. A mole of any gas, for instance, at roughly room temperature and standard pressure is 6.022×10^{23} molecules. That's 6,022 followed by twenty more zeroes, and equals a little over 24 liters of a gas. So even analyzing one billionth of one percent of an entire mole you'd still be counting trillions of molecules.

In any chemical reaction, it is essential to be able to figure out the exact measurements of all the ingredients. And we often use moles to do so. But we don't want to count each individual atom we need, because, as we've seen, that's a giant number. Instead we use molar masses: the mass of one mole of a pure substance.

Today we're going to measure the ingredients we need to make sodium iodide, a compound used in many radiation detectors.

JAMES NEVILLE: I'd like to show you how a sodium iodide radiation detector works. In my hand is a device built with sodium iodide crystal, and on the table is a small amount of radioactive material. In this case it's cesium-137, which is emitted from a nuclear reaction, as in a nuclear power plant. When I bring the device close to the radioactive material it will alarm.

DAVID SONG: Sodium iodide radiation detectors were key after a massive earthquake in Japan in 2011. The earthquake caused a powerful tsunami, which severely damaged the nuclear reactors at the Fukushima Daiichi Nuclear Power Plant. Radiation spread into the surrounding countryside and out across the ocean. Although food from farms and the sea was tested, consumers feared contamination. Radiation detectors were used by suppliers and consumers to provide scientific evidence that food was safe to eat.

To manufacture sodium iodide for radiation detectors we need to start with a balanced chemical equation.

To make sodium iodide from sodium and an iodine molecule, also known as diiodide, the equation looks like this: two Na plus I_2 yields two NaI. The coefficients let us know that there is a 1:1 relationship between sodium and sodium iodide and a 1:2 relationship between diiodide and sodium iodide. So if I want to make one mole of sodium iodide, I need one mole of sodium and one half of a mole of diiodide.

To measure out the right amount of our reactants, we can simply use the periodic table to look up the molar masses of sodium and iodine. Sodium's molar mass, rounded to the nearest whole number, is 23 grams per mole and iodine's is 127 grams per mole, so diiodide has a molar mass that is twice that number, 254 grams per mole. So, I want to mass 23 grams of sodium and half the molar mass of diiodide, which is 127 grams. Together they will combine to make 150 grams, or the molar mass of one mole of sodium iodide, just as the periodic table tells us it should be. By calculating molar masses you can be sure to have the right amounts of reactants to create the products you want.

[SEGMENT 4: Limiting Reagent]

DAVID SONG: So we're going to make some chocolate chip cookies today. I have all of my ingredients and the recipe. I add the proper amounts, mix everything together, put the cookie dough on the sheets, and put them in the oven. Now that I've made 24

cookies, just as the recipe said, I have all of these leftover ingredients. But I can't make any more cookies because I've run out of chocolate chips.

This happens all the time in chemistry. There is always one ingredient that runs out before the others. In chemistry we call that the limiting reactant or limiting reagent. Let's take a look at a chemical reaction, and ask yourself, "What is the limiting reagent?"

[SEGMENT 5: DEMO – Finding the Limiting Reagent]

DANIEL ROSENBERG: OK, today we are going to react methanol and oxygen. I'm going to start the reaction with a small piece of platinum wire, and the wire is going to act as a catalyst where the reaction takes place. And it is also an indicator, which shows us where the reaction is happening inside of that flask.

So the first thing we do is add methanol to the flask. It's already full of air. Four liters of air at 20 percent oxygen contains about .8 liters of pure oxygen. Now I'm going to add 10 milliliters of methanol. In this reaction one of the reagents is going to run out first, and that's what we call the limiting reagent. Is it going to be .8 liters of oxygen, or is it going to be 10 milliliters of methanol? In order to get this reaction going I'm going to heat up my catalytic wire, and then drop it into the flask. The air in the flask and the methanol vapor reacted in a flame. And now they're reacting on the wire, and the heat from that reaction is keeping that wire glowing orange hot. So in the system, which is going to run out first: the methanol or the oxygen? As long as the top is open and air can get in it's not going to be the oxygen.

So to find the limiting reagent we need to have a closed system. And I'm going to cork the top of this flask, and we're going to wait and see what happens to the glowing wire. Now air can't get in the top, and it seems as if though the wire is slowly going out.

So what's the limiting reagent? We can see there's still plenty of methanol on the bottom of the flask, but the wire stopped glowing. There's no longer any oxygen in the flask for the methanol to react with. All that we have left is methanol. I started with 10 milliliters and it looks like I have about two and a half milliliters leftover. So what's the limiting reagent? It was the oxygen that was the limiting reagent.

[SEGMENT 6: Sustainable Chemistry]

At the Myriant Corporation in Massachusetts, scientists are working to help decrease the burden on our natural resources. Using the principles of stoichiometry, they are producing green chemicals.

SUSAN HAGER: We make chemicals that people use everyday. We just make our chemicals from a process that is more environmentally friendly. So, rather than using petroleum, which is a natural resource rapidly being depleted, we're using renewable resources.

Petroleum is used to make many common household products. But as populations continue to increase, so does the demand for the world's dwindling supply of this limited resource. So instead of using petroleum, the research team has engineered a process to use sugar and bacteria to make chemicals. These renewable resources are used to create a chemical called succinic acid.

SUSAN HAGER: Succinic acid goes into the production of a large number of consumer applications that people know and use everyday. So everything from plastic bottles to paints that you would use to paint the inside of your house to making tires that go on your car.

Creating succinic acid is a two-part process. The first step is fermentation. In this stage, sugar, along with carbon dioxide and ammonia, is fed to *E. coli* bacteria and turned into ammonium succinate.

TAMMY GRABAR: This is basically a small fermenter, and you can see in here that there's a media that has sugar and our bacteria that's being stirred. And basically what we want to look for is the sugar being consumed and ammonium succinate to be produced. And in order to determine the rates at which that's happening, we just take samples every hour or so, and we can analyze, at any given time, the concentration of the sugar and the concentration of the ammonium succinate being produced.

After the team creates the ammonium succinate, they are ready for step two of the process. Here, sulfuric acid is added to the ammonium succinate and reacts to create two products. One is ammonium sulfate, which is used in fertilizer, and the other is the succinic acid.

CHARLISS DENNISTON: So here in our beaker we have some of our ammonium succinate broth, and we're going to be adding some sulfuric acids, some concentrated sulfuric acid, in order to have a chemical reaction where we move our ammonium succinate into ammonium sulfate and we get succinic acid, our desired product, out of our chemical reaction.

To figure out how much sulfuric acid needs to be added to the ammonium succinate to create the desired products, the researchers must start with a balanced equation. The same number of atoms of each element are on both sides of the equation. And in this equation, the ratio of the number of each reactant is 1:1. One mole of ammonium succinate plus one mole of sulfuric acid yields one mole each of ammonium sulfate and succinic acid.

CHARLISS DENNISTON: If we know how much ammonium succinate is in here, and we know the chemical formula for ammonium succinate, and the chemical formula of sulfuric acid, we can actually calculate the molecular mass of those compounds based on the atoms that are in each of those chemicals. And we can use those molecular masses to figure out how much volume of sulfuric acid we need to add in order to push our chemical reaction to completion.

So, this is our fermentation broth, our ammonium succinate, and we're going to measure out about 300 milliliters of this into our beaker. All right. And we calculated that we'd need about 12 milliliters of concentrated sulfuric acid to make our reaction go to completion. So we're going to measure that out as well.

If we didn't know exactly how much sulfuric acid we needed to push the reaction all the way to completion, and we didn't have enough sulfuric acid, we would still get some of our succinic acid product, but we would have wasted a lot of our ammonium succinate, not all of it will have reacted and converted to our succinic acid.

In chemistry, no reaction is perfect. One reactant will always run out first, leaving one or more reactants left over. The reactant that runs out first is called the limiting reagent. For Myriant, to reduce waste and maximize yield, they want their most valuable reactant to be the limiting reagent.

CHARLISS DENNISTON: So in this chemical reaction, our ammonium succinate is our limiting reagent, because there is only so much ammonium succinate that our *E. coli* will produce. So we want to make sure that all of that ammonium succinate gets used up in the chemical reaction. It's easier and cheaper for us to buy sulfuric acid, and so we want to add a little bit more of the sulfuric acid to make sure that all of our limiting reagent gets transformed into our succinic acid, our product.

Balancing chemical equations, understanding molecular mass and taking into account the limiting reagent, are all essential in creating and mass-producing an environmentally friendly succinic acid.

SUSAN HAGER: One of the things that's really important about producing bio-based chemicals is precision. And that's because our customers aren't going to give us a break just because the products we're producing are made from sugar. They expect that when they get bio succinic acid from us that it meets the same stringent requirements for purity and performance as a product that they're used to using from petroleum. So we need to make sure that what we're doing in the lab, we can bring through to commercial scale, and we can carry that precision through at each step of the process.

[WRAP-UP]

DAVID SONG: Balancing equations, figuring out the masses of our ingredients, and using the limiting reagent to our advantage, are all necessary tools for chemists to plan and make their chemical reactions. Without these resources in our tool belts we can't efficiently perform the reactions we want to produce chemicals from sustainable products, or to create energy.

[END]