Chemistry: Challenges and Solutions
Unit 2: The Behavior of Atoms
Phases of Matter and the Properties of Gases
Hosted by Mala Radhakrishnan

[Tease]

Increase the temperature of ice, and it turns into liquid water. Raise the temperature more, and the liquid turns into a gas we call steam. We've been taking advantage of matter's ability to change for thousands of years, but it is only relatively recently in the history of science we've understood what's happening in the different phases of matter at the molecular level. These physical changes can help us to think about how we power the world in a cleaner way, including how to use hydrogen more efficiently as a fuel for powering our cars.

PETER WONG: It's important to understand the phases of hydrogen so that you can think about ways of putting hydrogen closer together.

By understanding the phases of matter, we can use fossil fuels without contributing to global warming by taking the carbon dioxide normally released into the atmosphere and storing it deep underground.

CHARLES BRANKMAN: Without understanding the phases of matter we would not be able to even consider storing carbon dioxide.

It's all about how atoms behave in the different phases of matter.

[Title: Chemistry Unit 2 - The Behavior of Atoms]

MALA RADHAKRISHNAN: The phases of matter: solids, liquids, gases, are concepts we begin studying in elementary school. Understanding how matter can change from one phase to another is our first step toward understanding the behavior of atoms.

[SEGMENT 1: Phase Diagram]

MALA RADHAKRISHNAN: Hi, I'm Mala Radhakrishnan, a professor of chemistry at Wellesley College. To better understand how phase changes occur, we can use a handy tool called a phase diagram. Any substance can be represented by a graph whose axes are pressure and temperature. Such a graph can give you a rough idea under what conditions the substance is a solid, a liquid, or a gas. Temperature is essentially a measure of kinetic energy, which is related to how much the atoms are moving around.

At low temperatures the kinetic energy is low and so atoms don't have enough energy to overcome their attractions for each other. As a result they end up being very close together and the matter tends to be a solid. At high temperatures however, atoms now have enough energy to overcome their attractions for each other and so they can become a gas moving all around and taking up a lot more volume than a solid or a liquid.

At a particular pressure we can trace the transition from solid to liquid to gas of a given substance. We start with a solid. As the temperature is increased the atoms or molecules now have enough kinetic energy to somewhat overcome their interactions for each other and the substance becomes a liquid. If you further increase the temperature, the atoms or molecules essentially break free from each other because they have so much kinetic energy to overcome their interactions and the substance becomes a gas. The points at which a substance goes from being a solid to a liquid, or from a liquid to a gas, are known as the melting point and the boiling point respectively.

For a substance that is a gas we can further increase the temperature and the atoms and molecules will move even faster and take up even more volume than before. We can visualize the effect of temperature in a model of a gas using golf balls as gas molecules

[SEGMENT 2: DEMO - A Model of a Gas]

DANIEL ROSENBERG: We've got a model of a gas here. It's a constant pressure vessel, and we're going to increase the temperature by moving those golf balls around faster and faster. So I am going to raise the temperature of our gas, and we're going to watch and see what happens to the volume. The temperature is going up; molecules are moving faster; and the volume goes up. Now what happens when I lower the temperature is the temperature goes down. So does the volume.

MALA RADHAKRISHNAN: To follow the path from one phase to another we can also change the pressure. Changing the pressure changes the volume, which is the amount of space the atoms have to move in. At low pressures with temperatures we can experience in our atmosphere, matter tends to be a gas. Increase the pressure, and matter has less space to move around, and transitions to a liquid.

Every substance, including carbon dioxide has its own phase diagram indicating under which conditions it is a solid, a liquid, or a gas. With solid carbon dioxide we can make a phase change by increasing both temperature and pressure.

DANIEL ROSENBERG: Now we're going to make a phase change. We're going to take dry ice, which is solid carbon dioxide, and we're going to turn it into a liquid. Now dry ice is called dry ice because when it melts, it doesn't turn into a liquid, it turns straight into gas. So if we leave this here, no liquid, just gas.

This can be seen in the phase diagram of carbon dioxide. At atmospheric pressure, as you increase the temperature, it turns directly from a solid to a gas.

But if we put the dry ice under pressure, the phase diagram shows that dry ice should act like regular ice and turn into a liquid. So we're going to put it under pressure with this vice, inside this little tube. Now the tube is sealed. The carbon dioxide is turning into a gas. The gas is filling up a constant volume. That means the pressure is going up.

But what is making the pressure increase? Is it the vice? Or is it something that is happening inside the tube? The pressure is not increased by the vice. The vice just acts as a lid and keeps the volume fixed.

Inside the tube, as the temperature of the dry ice rises, some of it changes from solid to gas. The gas particles take up more space than the solid particles, and therefore increase the pressure in the tube.

As the pressure goes up we'll reach a point where the carbon dioxide can exist as a liquid, and indeed as we watch it, this crumbly, white material is turning into, what look like little ice cubes, and melting. It's no longer dry ice carbon dioxide, its actually liquid carbon dioxide. It's the phase that you can't get at atmospheric pressure, only under high pressure.

But does that mean as a liquid it's going to stay a liquid if I release the pressure? Let's find out. Carbon dioxide can't exist as a liquid at atmospheric pressure. Ta-da. Ta.

MALA RADHAKRISHNAN: For any substance it's a combination of temperature and pressure that decide what phase it will be in. Each phase has the same number of particles, but the space between the particles is different – much, much different for a gas as compared to a solid or liquid.

[SEGMENT 3: Hydrogen Storage]

MALA RADHAKRISHNAN: Understanding how atoms behave in different phases can help us to think ways to create cleaner energy, for things like this car I'm driving. Most cars run on gas, which releases carbon dioxide into the atmosphere, contributing to climate change. But what if we could run our cars on something that wasn't bad for the environment?

Peter Wong of Tufts University is thinking about how we can power our vehicles with hydrogen instead of fossil fuels. Hydrogen is used in fuel cells, devices that use hydrogen and oxygen to create electricity.

PETER WONG: So what's really nice about fuel cells is that it uses hydrogen, oxygen from the air, it creates electricity, and the only by-product is water, which isn't harmful to our environment. So we could make hydrogen fuel-cell cars right now, however the gatekeeper for the technology to be used is the storage of the hydrogen.

How we produce hydrogen is also an important obstacle in producing cleaner energy for transportation, but Wong is concentrating on the challenge of getting as much hydrogen into one storage space as possible. Hydrogen, in the form of a gas, is possible, but not economically practical for powering a car. The atoms of a

gas as compared to those in a solid or liquid just take up too much space to have a high enough density, or atoms within a given volume to produce enough energy. Wong's solution is to add solid material in the form of nanofibers inside a container. This material is manufactured into sheets that fit inside. These sheets add surface area to the interior of the container, which has the same effect as increasing the volume of the tank, allowing more hydrogen atoms to fit inside.

PETER WONG: So the challenge is to get more hydrogen molecules into this fixed volume without increasing the weight too much.

Wong is searching for solid materials that will trap the hydrogen molecules, effectively making the hydrogen gas molecules part of a solid. Using a specific bacterial cellulose, gluconacetobacter xylinus, as a starting point, Wong creates nanofibers that could be engineered to be installed inside a tank.

PETER WONG: So, it's found in nature in the Philippines. It's prevalent as a way of making a dessert called "nata de coco." So, it comes from coconut milk. And so what we're looking at is a way of taking the gas phase, having it connect with a solid material and finding its way to a storage site.

Wong and his team have to heat the bacterial cellulose, which drives off hydrogen and oxygen, leaving only carbon behind – which increases the probability of the hydrogen atoms being trapped by the material.

PETER WONG: It is heated without burning, so it doesn't just go away into the atmosphere, but actually stays as a solid material, but now it's just carbon. All the other components have been driven off through the heating.

To the naked eye, you can't see the fibers. So what we're looking at here is a scanning electron micrograph of the carbon nanofibers. Here, we in fact can see the fibers. Each one can be several nanometers in diameter. And it stretches for, oh about a micron or so, which seems pretty small, but in terms of the scale are very long strands. And so, this is a good geometry because it has a high surface area for that volume. But if we did not have this material here, and we had hydrogen in the tank they would be moving around, and as you try to put them closer together they would try to push back. And so you can only get so much hydrogen into that volume. When we put this carbon nanofiber inside, now the hydrogen can come and they'll still push each other, but some will find its way onto the surface of the carbon nanofiber. And they can sit there and not interact as much with the gas phase. And so the gas phase hydrogen molecules have more room, so we can then put more hydrogen atoms molecules inside the same volume.

To see if the material will allow for more hydrogen atoms to fit within a fixed space, Wong can run a simple test. Here Wong simulates how the experiment is conducted.

PETER WONG: What we do is we take some of the material put it in this system. Then if we connected hydrogen to it, filled it with hydrogen, and monitored the pressure, what we hope to see is a drop in pressure over time, and that correlates to an increase in hydrogen molecule storage in the material.

The results of these tests show the potential to increase the number of hydrogen molecules by a factor of 1,000 when compared to having no nanofibers inside the container. This improves the current technology of hydrogen-powered cars, but does not yet reach the efficiency goals thought necessary to make hydrogen economically feasible.

PETER WONG: So 1,000 times storage sounds great, but our target, how much hydrogen we need to make the car practical, is about 10,000 or a 100,000. So there's still a need for a lot of research and development to hold that amount.

[SEGMENT 4: Gas Laws]

Mala: In order to understanding and predict how gases behave, we first need to understand relationships between pressure, volume, and temperature.

During the 17th, 18th, and 19th centuries, scientists introduced key concepts relating to the behavior of gases.

In the 17th century, chemist Robert Boyle focused on what he called "the spring and weight of the air." Using a curved glass tube with air trapped inside by mercury, Boyle observed that when he added more mercury to the open end of the tube, the volume of air at the sealed end was compressed. The increased pressure from the increased amount of mercury changed the volume of the gases in the end of the tube; increasing the pressure reduced the volume. The opposite is also true: decreasing pressure increases volume. The results of this experiment became known as Boyle's Law.

In 1802 Joseph Gay-Lussac published Charles' Law, because it referenced work by Jacques Charles. Stating that the volume of a gas is directly proportional to its temperature: temperature and volume will increase together or decrease together. In the gas phase, particles completely fill the shape and volume of a container, including that of a balloon. According to Charles' law, when heat is added to increase the temperature, the volume of the balloon also increases.

Meanwhile, in 1811, Italian chemist Amedeo Avogadro proposed that equal volumes of gases under identical temperature and pressure conditions contain the same number of particles, regardless of the identity of the particle in the gas.

And everything came together in 1834, when Emile Clapeyron combined all of these laws and created the Ideal Gas Law. The law summarizes the roles of pressure, volume, and temperature in describing the behavior of a gas, and can

be summarized as PV = nRT. in this equation, R is a mathematical constant and n represents the number of particles of the gas.

The ideal gas law is a model that accurately describes how most common gases behave within the temperature and pressure ranges in which we live.

[SEGMENT 5: DEMO - Volume = Temperature]

DAN ROSENBERG: Now, I am going to demonstrate the relationship between volume and temperature.

So I'm going to take a balloon and fill it with helium gas. So all those helium atoms are bouncing around the inside of the balloon. Now when I tie the knot, and the number of atoms in this system is fixed. And it's the atoms moving, bouncing against the wall that make the pressure that keeps that balloon inflated.

Now I'm going to reduce the temperature from room temperature to liquid nitrogen temperature. Much colder, the atoms will be moving more slowly so they won't be bouncing against the walls of the balloon. So if anything, this balloon should shrink. The gas inside the balloon is cooling down and indeed its volume goes way down. So, that's cold helium gas. What happens if I increase its temperature by taking it out of the liquid nitrogen? Let's see what happens then. Its volume increases because its temperature increases and it rises just like any helium balloon.

As the temperature of the atoms inside the balloon is decreased by the liquid nitrogen, the volume decreases. And when the balloon is no longer in contact with the liquid nitrogen, the temperature of the atoms inside the balloon increases, as does the volume.

P V equals n R T.

[SEGMENT 6: Supercritical fluid]

MALA RADHAKRISHNAN: The ideal gas law works pretty well. It explains how gases behave in many conditions we experience. The air around me, for example, can be described fairly accurately by the ideal gas law. But the ideal gas law can't be broadly applied to everything because of course not all matter is gaseous, and not all gases are ideal.

As temperature and pressure change enough, eventually gases become liquids and solids. If temperatures and pressures are sufficiently high, gases or liquids can turn into a fourth phase called the supercritical fluid.

On a phase diagram the conditions for super-critical fluid begin at what is known as the " critical point." Past this point, matter is no longer a liquid or a gas, but somewhere in between, meaning a given amount takes up more volume than a liquid but less volume than a gas.

It is this supercritical phase that is allowing C12 Energy, a small startup company in Berkeley, CA to think about a way to combat climate change. One of the major contributors to climate change is carbon dioxide, a heat trapping gas in the atmosphere. It is produced as a by-product when we burn fossil fuels to make energy.

Fossil fuels are going to be used for decades. The problem is, what do we do with the carbon dioxide emissions? C12 Energy is thinking about preventing the carbon dioxide from reaching the atmosphere by storing it.

It's not sensible to store carbon dioxide as a gas. It just takes up too much space, and its too expensive to store as a liquid or solid, so C12 Energy is thinking about storing it underground as a supercritical fluid.

It just so happens that the temperature and pressure hundreds of meters underground match the conditions under which carbon dioxide becomes a supercritical fluid.

ANTONIO BACLIG: A supercritical fluid is a phase that's like a liquid and a gas. Basically, you become this fluid that's dense like a liquid, but it expands to fill its container like a gas. And so, for CO_2, there's a big density benefit. In a given volume, we can fit more CO_2 in.

Deep underground, as a supercritical fluid, CO_2 takes up less than one percent of the volume of CO_2 in a gas phase at ground level. That's a lot more space to store unwanted CO_2. To make sure it stays underground, the team looks to find ideal geologic conditions.

CHARLES BRANKMAN: So here we have a schematic of a cross-section through the Earth at a site in Central Illinois. And represented by the different colors are the different layers of rock that are present in the subsurface. And the target for geologic storage of carbon dioxide is to find rock where you can inject the CO_2 and it will remain there permanently. So what we're interested in here is the reservoir rock down, it's about 7,000 feet deep and it's composed of sandstone, the sandstone reservoir. This rock is actually between 10 and 20% empty space. And it's that empty space within this rock, which the CO_2 will, once its injected, flow through. And because it's buoyant it will try to go to the highest point, so it will try to get to this peak. So above that we have a rock unit represented in the orange, which is shale or a mud rock. This is very impermeable, and fluids basically can't pass through these rocks. So the combination of the sandstone underneath with the impermeable cap rock above forms that geologic trap for the CO_2.

So this really represents only the downstream portion of the project, so not shown in this figure would be some sort of industrial facility, a coal-fired power plant, a refinery, an ethanol plant, something that you're generating CO_2 as a byproduct of some industrial process. Essentially what happens is the CO_2 will come along the surface through a pipeline in the supercritical state to the wellhead, it will travel down the injection well into this injection zone and fill up the pore space, the empty space between the grains of rock and this reservoir. And it will be trapped and kept from migrating upwards by this overlying shale cap rock or seal unit.

Because of the buoyancy of the supercritical fluid, the shape of the formation is also important. So Brankman analyzes 3-D renderings of a potential site.

CHARLES BRANKMAN: So here we're looking in detail at the top of this reservoir surface and this line represents the injection well. So the CO_2 will actually come down through this injection well and into the reservoir and once it's there it will be prevented from moving further upwards by the overlying shale unit. And then as it fills in the crest, the additional CO_2 will essentially fill in from the top of this structure further down.

It's exactly like pouring liquid in a bowl but flipped upside down. If you poured water into a bowl you'd be filling the base of the bowl and successfully filling it up to the rim. Here you're flipping the bowl over but you're pouring in material that wants to go to the top. So you're filling the crest first and then you're going to – as you fill it up it's going to migrate further and further down.

To project the path of the supercritical fluid over time, the C12 team creates various simulations of the CO_2 injections at different sites.

ANTONIO BACLIG: So this is a video of a simulation that we ran of CO_2 being injected into a sandstone layer that's about a couple of kilometers under the surface.
So this is the sandstone here, this green. And this is just a cross-section but you can see the surface of it is shaped sort of like a long bowl. Now above it is a shale layer, so that's something that's going to be impermeable to CO2. So now I'm going to start injecting CO_2 and the CO_2 is a supercritical fluid at these conditions and it shows up in red. That's just the concentration of the CO_2 in the reservoir. What you're seeing is the end of our injection actually, this is 30 years after we started. We injected a lot of CO_2 and it mostly went into these very permeable layers. We injected throughout the whole length of it, but because certain layers in the rock were more permeable than others the CO_2 had these preferred flow paths. What I'm going to show you is what happens after 500 years. And you're seeing it pull upward. Essentially what happens is that the CO_2, since it is buoyant, it gets pushed upward to the top of our reservoir and it forms this bubble at the top of the reservoir, that because we have this structure will just stay like that for the next 500 or 1,000 or however many years. We always run our simulations out, hundreds of years because we want to make sure that we're not going to cause problems for future generations

Much more geologic research at power plant sites around the world still has to be done, but without the knowledge of how and where supercritical fluids exist, putting carbon dioxide underground instead of in the atmosphere would not even be an option.

CHARLES BRANKMAN: Without understanding the phases of matter we would not be able to even consider storing carbon dioxide.

[WRAP-UP]

MALA RADHAKRISHNAN: Now that we have a better understanding of how atoms and molecules behave in the different phases of matter we begin to think about chemical interactions. The relationship between matter and pressure, volume, and temperature, provide an important foundation in learning about chemical reactions and how we can manipulate them to have a real impact on the world we live in.

[END]