# Chemistry: Challenges and Solutions
## Unit 7: The Energy in Chemical Reactions
## Thermodynamics and Enthalpy
Hosted by Nicole Labbe

*[Tease]*

**Narrator: Sometimes, when chemical reactions occur, it is a sight to behold. And a dramatic illustration of a basic function of all chemical reactions: they transfer energy. Often that energy is being transferred through heat . . .**

DANIEL ROSENBERG: This is the flame tornado.

**Narrator: And we take advantage of that all the time - to cook food, heal wounds, and simply to get around. Understanding how and why energy moves is achieved through the study of thermodynamics. So whether it is building more efficient cars . . .**

KEVIN CEDRONE: In my work I use thermodynamic principles all the time. What's interesting here is that instead of doing the chemical reactions in a lab in a beaker, this is being done in real time in an engine.

**Narrator: Or searching for alternative fuel sources . . .**

GRETCHEN SASSENRATH: We hope to convert plant products into a useable biofuel. A lot of that requires understanding of thermodynamics and thermochemistry.

**Narrator: Our ability to move forward and advance society through chemistry relies heavily on our ability to measure, predict, and control the heat and energy of chemical reactions.**

*[Title: Unit 7 – The Energy in Chemical Reactions]*

NICOLE LABBE: When you set fire to a piece of wood, you are not creating energy; you are simply converting it from chemical energy to light and heat energy. This is an illustration of the First Law of Thermodynamics, which tells us that energy can neither be created nor lost, only transferred from one form to another.

Hi, I am Nicole Labbe; I'm a Chemical Engineer, and I research how fuels burn in so we can make them safer to use.

My interest in chemistry and thermodynamics started when I was a kid. When I saw something burning, like a campfire, I would stare at the flames. Not that different than most kids . . . but I always wondered why the wood that normally wouldn't do anything was burning.

In chemistry, we care a lot about the heat involved in chemical reactions. And although heat itself is one of the ways energy gets transferred, often energy is not the terms chemists use to describe the heat. Instead, we use the term enthalpy. We use enthalpy instead of energy because we are not just interested in the energy being released, but also the effect that energy has on the pressure and the volume of the system we are studying. Enthalpy takes that effect into account. It is defined as the energy plus the pressure times the volume.

*[SEGMENT 1: Exothermic Reactions]*

We call reactions that release heat exothermic reactions. In an exothermic reaction, the enthalpy of the reactants, what you begin with, is greater than the enthalpy of the products, what you end up with. We describe this as a negative change in enthalpy.

There are many fantastic examples of exothermic reactions in the world, let's take a look at one.

*[SEGMENT 2: Demo – Flame Tornado]*

DANIEL ROSENBERG: This is the flame tornado. It's an example of an exothermic reaction. And an exothermic reaction is a reaction that releases heat.
Now, we don't need the turntable and the screen to show you the actual reaction, it's the reaction between isopropyl alcohol and the oxygen in air. And I can do this reaction right on the table-top.

So the enthalpy that's released from this exothermic reaction is coming off in the form of light and heat. And we can take advantage of that by running the reaction inside of this cylinder.

Now it's the same exothermic reaction on the inside of the cylinder as it was on the outside, but when I spin the cylinder, more air moves in to the cylinder and the reaction happens at a higher rate. It turns into a flame tornado. In this reaction the enthalpy is negative; the products have less enthalpy than the reactants.

*[SEGMENT 3: Endothermic Reactions]*

NICOLE LABBE: But chemical reactions don't just release heat, they can also absorb it. And this heat absorption is a reflection of the reactants having less enthalpy than the products. In this case, it still takes enthalpy to break the bonds but we don't get as much enthalpy back when we form the new bonds. We describe these reactions as having a positive change in enthalpy. They are known as endothermic reactions. Let's take a look at an example of an endothermic reaction.

*[SEGMENT 4: Demo – Heat Absorber]*

DANIEL ROSENBERG: This is the reaction between barium hydroxide and ammonium chloride. Now, it's pretty obvious when a reaction releases heat to its surroundings. How are we going to tell that it's absorbing heat? And the way I am going to do it is by putting a little bit of water underneath this beaker and running the reaction on top of this block.

So I am going to add the ammonium chloride to the barium hydroxide. Now I'm stirring two solids together, but one of the reaction products is water. And so very quickly these two dry solids become a slush, and then a solution. One of the other products of this reaction is ammonia, and so if I take a little whiff I can smell that ammonia, and I know this reaction is going as scheduled.

So how do I know that this reaction is endothermic? Well, remember how I squirted water on the block before I started the reaction? And so, now when I lift up the beaker, the block comes with it. The reaction has frozen the water to the block. The products have more enthalpy than the reactants, and they took that enthalpy in the form of heat from the surroundings. And part of the surroundings was the water in between the beaker and the block. And that water is frozen solid . . . pretty cool.

*[SEGMENT 5: Measuring Heat]*

NICOLE LABBE: The relationship between heat and the change in enthalpy is an important one in chemistry because under constant pressure, the change in enthalpy is equal to the heat.

The environment we live in is under constant pressure, so that makes it easy for us to measure the change in enthalpy of a reaction.
We can do this using a coffee cup calorimeter.

A calorimeter is simply anything used to measure heat, and Styrofoam cups are useful because they minimize heat loss to the surroundings.

Here, I take a coffee cup filled with water, and I insert a thermometer to find out what the temperature is – it is 23 degrees Celsius. Then, when I add sodium hydroxide to the water, let's see what happens to the temperature. We see that pretty quickly the temperature starts to rise and it rises to 28 degrees Celsius. That's five degrees above the starting temperature.

So, the sodium hydroxide, when mixed with water, causes an exothermic reaction and releases heat. So where does that heat go? It can't just disappear, and that's why we see the temperature rise. We can take that temperature change and relate it back to calculate the actual change in heat. This is just a conversion from temperature, which we measure in degrees, to enthalpy change, which we measure in calories or joules.

*[SEGMENT 6: Mississippi Biofuels]*

**Narrator: Scientists use calorimeters all the time to measure heat. And Gretchen Sassenrath, of the Agricultural Research Service in Stoneville, MS, is leading a study for the US Department of Agriculture, where they use calorimetry to figure out which crops could best serve as a potential alternative fuel source.**

GRETCHEN SASSENRATH: We need energy to run all of society. Most of the fuels that we're using right now are fossil fuels, which have negative environmental consequences and they're limited. So, we hope to be able to generate biofuels in a way that has a lower environmental impact.

So, the first thing we wanted to do was just look at energy potential of traditional crops that are already grown in Mississippi: cotton, corn, soybeans, winter wheat, and rice.

**Narrator: Sassenrath is not just testing the harvestable portion of the crops, but all of the plant material in the field. The hope is that we can access the energy in the crop residue, which is often thrown away or burned.**

GRETCHEN SASSENRATH: They're burning the residue already. This is a perfect opportunity to make biofuels that would not be competing with a food source.

**Narrator: In addition to the major crops in Mississippi, Sassenrath included sweet potatoes, which only make up about 0.3% of the state's total production.**

GRETCHEN SASSENRATH: Small farmers grow sweet potatoes. And what I'm looking at is not a million dollar solution; I'm looking at a ten-dollar solution. What can we do on the farm that is going to enhance the rural community, give the farmers an economic boost either by having them be able to sell their product for something, or have them produce biofuel on the farm so that their fuel costs are reduced by them producing their own fuel.

**Narrator: Rockiell Woods runs a demonstration farm for Alcorn State University and works with Sassenrath on improving productivity on small farms.**

ROCKIELL WOODS: When a farmer harvests sweet potatoes, they look in terms of choosing a U.S. number one, which is the most desirable sweet potato. They also look at the number twos and the jumbos. Here we have a potato sticking out right here. There, you have a perfect number one! Some of the undesirables would be some of the culls, the cuts, the bites that are not desirable to the eye, to the market. But this sweet potato would be good for the energy process. It would make a farmer feel like that he's gonna harvest and he's gonna make money on both ends. It's a guaranteed win-win situation.

**Narrator: Sassenrath and her team collected samples of sweet potatoes and all the other crops and brought them to a lab at William Carey University to check the energy content in a calorimeter.**

JONATHAN CLEMENT: Once we get the sweet potatoes in from the harvest, we clean them, allow them to dry, and then I slice them to pieces. The process that we execute is the same for any crop that comes in.

**Narrator: After the sample is sliced, it is put in an oven for three days to remove any moisture which would affect the energy reading in the calorimeter.**

JONATHAN CLEMENT: After it's dry we take the individual pieces; we break them into smaller pieces in a food processer. We then take this dust and form it into a pellet. And now it's ready to test in the calorimeter.

SUBHI TALAL YOUNES: First, we need to weigh the pellet very carefully. Ultimately, we are looking for calories per gram of plant material in order to determine total energy content and extrapolate that back to the original plant.

**Narrator: The calories they measure are chemistry calories, a bit different from the calories we are familiar with.**

SUBHI TALAL YOUNES: Most people when they hear the term calorie are actually speaking of food calorie, which is one thousand chemistry calorie. One chemistry calorie is the amount of energy required to raise one gram of water by one degree Celsius.

**Narrator: Once they have the exact weight of the pellet, they can test it in a bomb calorimeter. Bomb refers to the container that holds the sample.**

SUBHI TALAL YOUNES: First we need to get a piece of nickel chromium alloy wire, and run that on top of the pellet; that will connect to our ignition source and ignite the pellet when we're ready. Now, I have to make sure of two things: first, that the wire is in physical contact with the pellet, second, that it's not touching this metal rim; otherwise we'd create a short circuit.

**Narrator: Once the wire is in place, the pellet is placed inside the container and the bomb is sealed.**

SUBHI TALAL YOUNES: Our next step is to purge all the atmospheric gases out of the bomb in order to prevent waste products from forming, which would take away from our total energy content, and to pressurize the bomb with pure oxygen to make sure that our pellet completely combusts.

**Narrator: The bomb is then placed inside another container filled with two liters of distilled water. When the pellet combusts, the heat from that reaction will heat up the bomb, which in turn heats up the surrounding water. The temperature increase that they measure is the temperature increase of the water.**

SUBHI TALAL YOUNES: Okay, we're ready to go; the last thing is to put the lid on. In the lid, we have the thermometer, which will of course give us the temperature of the water, which we read here. And we also have a stirrer, which will make sure that the temperature of the water is the same throughout.

We're going to turn on the motor to stir the water, and then we'll get a reading of the water before we fire the calorimeter for at least six minutes to make sure we have a good baseline temperature.

We've recorded the temperature for six minutes, and we're ready to ignite.

All right, our red light flashed very briefly; that tells us we had a successful ignition.

**Narrator: After ignition, the temperature is recorded every thirty seconds until it plateaus and then cools down. To get the calorie measurement for the sample, they take the temperature difference between the water before ignition and the highest temperature after ignition.**

SUBHI TALAL YOUNES: Now we're venting the pressure, and this is the most exciting part. It's when you get to open it up and see what's actually left. Now this sample worked beautifully; I mean just perfect. We have a little bit of what we call ash content left; it may seem insignificant, but we actually need to measure it because we need to subtract it from our final calculations of energy content.

**Narrator: But the weight of the remaining ash, and the temperature change of the water, are not the only measurements needed to calculate the energy content of the sample. The calorimeter, as well as the wire used to ignite the sample, each have a certain heat capacity, which is basically the amount of heat they will absorb.**

**Only by taking all of these different variables into account can they accurately determine the energy content of the sample.**

**For a sweet potato, they found that one gram contained 3966 calories, or 3.966 food calories. And when they extrapolate that out, the sweet potato had more energy per acre than any of the other crops measured.**

GRETCHEN SASSENRATH: That was pretty exciting, because it would benefit the small farmers and also the rural communities by having a crop that they can grow locally and could be used locally for fuel production.

This work is so cool; this is so much fun, because there's so many questions and potential impact that we can make.

And understanding thermodynamics is really important, because we need to understand energy and energy flows and energy conversions so that we can continue to support society and we can continue to grow, not just in America but in the world.

*[SEGMENT 7: Bond Enthalpy]*

NICOLE LABBE: Burning things in a calorimeter is an effective way of understanding reactions on a fundamental level, but it’s not the only way. Chemists can calculate the enthalpy of a chemical reaction by knowing what the reactants and products are in that reaction. To do this, a chemist needs to know the enthalpy of each individual bond.

For hundreds of years, chemists have been doing experiments to find out what the bond enthalpies are for specific bonds in molecules, and now we have tables that show us exactly what those values are. So, if we know the structure of a molecule, even a molecule we have never done a reaction with before, we can calculate its enthalpy. And this can help us figure out how it may behave in a chemical reaction.

This is something that I do all the time in my research with hypergolic rocket fuels. Hypergolic fuels are fuels that do not need a spark to ignite. Instead, they react as soon as they touch another chemical. They could be useful in military applications or to power satellites.

One such fuel is monomethylhydrazine, or MMH. When we combine MMH with red fuming nitric acid, we get an incredible reaction, but we want to know what dangerous fumes can come from this, and we want to figure that out without having to actually burn the fuels. And we can do this using bond enthalpies.

This is the overall reaction between MMH and nitric acid. But really, these molecules don’t spontaneously turn into these molecules.

They go through thousands of different reactions along the way, and they form lots of different species. Even this is a very simplified version of what actually happens.

By knowing the bond enthalpy of the reactants, I can calculate the odds of which bonds will break, and much like a meteorologist can forecast the different paths of a hurricane, I can create models that can accurately forecast the pathway this reaction will take and what the products of that reaction will be.

It is pretty complicated to deal with bond enthalpies at this level, but it’s really cool to think about all of the information that is available just by knowing the chemical formula of a reaction.

We have spent a lot of time talking about how heat is related to the transfer of energy, but energy transfers can take on another form – work. In thermodynamics, work is defined as any change in the energy of a system that is not a heat transfer. Work often takes on the form of mechanical energy, and work can create heat. But heat can also create work.

During the days of steam power, scientists wondered if they could design an engine that would perform this heat to work conversion with one hundred percent efficiency.

In 1824, with the hope to better understand the fundamentals of this heat/work relationship, a French engineer named Sadi Carnot developed a theoretical piston engine. In this idealized engine, no heat was lost through the engine walls or because of the friction of the moving parts. Carnot realized that even in this hypothetical model, it is impossible to convert all of the heat into useful work.

This idea eventually lead to the Second Law of Thermodynamics, which tells us that some energy will always be wasted so that you can never break even.

*[SEGMENT 8: Fighting the 2nd Law]*

**Narrator: At MIT's Sloan Automotive Lab, researchers like Kevin Cedrone are trying to get as much work out of an engine as possible.**

KEVIN CEDRONE: The focus of my work is making engines cleaner and more efficient. My Dad was an auto mechanic, and so I used to work with him in the garage from the time I was about 4 or 5 years old. And I've got a motorcycle that I ride and work on all the time, and it's a kind of a fun way to take what I do in the lab and apply it to real life. This is a GM ECOTEC four cylinder, two liter engine. This engine is where I do more than ninety percent of my research. One of the things we'll look at today is just how important it is to get the spark plug to spark at the right time, and what kind of impacts that has on efficiency.

**Narrator: Spark plugs control the timing of when the chemical reaction occurs inside an engine. Internal combustion engines are driven by pistons that move up and down in a chamber. During the compression stroke, the piston compresses a mixture of fuel and air, raising the temperature and pressure inside the chamber. As the piston nears the top of the chamber, the spark plug sparks, causing combustion, which is an exothermic chemical reaction between the fuel and air that releases heat and drives the piston down.**

**The reason spark timing is so important is if the spark plug ignites too soon, a lot of the heat from the reaction will be lost in the walls of the engine before it can be used as work to move the piston down. If the spark happens too late, not all of the energy is extracted and it stays in the exhaust, resulting in hotter exhaust gas, and more heat loss to the engine walls. On the ECOTEC engine, Kevin can control the spark timing with a computer.**

KEVIN CEDRONE: So let’s start up the engine, and we’ll see how the spark timing affects the efficiency of the engine. So, this is a PV diagram; it’s a tool used in thermodynamics to look at the work extracted in a cycle.

**Narrator: PV stands for Pressure and Volume. In thermodynamics, the amount of work done by a system is equal to the change in volume times the pressure. This diagram is a graphical representation of what is happening inside the combustion chamber.**

**To determine the engine’s efficiency, Kevin focuses on the compression and expansion strokes. During the compression stroke, the pressure goes up as the volume of the chamber goes down. Then, once the spark plug sparks, the pressure shoots up but then drops as the piston is driven down the chamber, which also increases the volume.**

KEVIN CEDRONE: So, the size of this upper loop, this upper loop here, represents the amount of work. So, the larger the area inside this loop, the more work that the engine is producing, and the smaller the area of that loop, the less work that the engine is producing. And as we change spark timing we’ll see the loop grow and shrink.

**Narrator: In addition to pressure and volume measurements, Kevin measures the temperature of the exhaust. Hotter exhaust means wasted heat that was not used as work.**

KEVIN CEDRONE: Right now the spark is firing 25º before the piston reaches the top of the cylinder.

**Narrator: 25º refers to the angle of the crankshaft, which is connected to the piston, and rotates as the piston moves up and down. If you think of this rotation as a circle, the spark is firing 25º before the crankshaft has reached the full top position.**

KEVIN CEDRONE: With the spark at 25º before top center, we see an exhaust temperature of 502º Celcius. If I change the spark timing to 10º before top center, combustion started significantly later, so we can see that the top loop got smaller, and we’re missing area up here, so there is less work coming out from the piston, and the temperature went up. The energy that was left over that the piston did not extract, came out of the engine as thermal energy instead.

So with later spark timing, the engine runs less efficiently, and I have hotter exhaust as a result.

**Narrator: For this set of conditions, 25º before top center is the optimum spark timing. These results not only shed light on the efficiency and safety of the engine, but they offer a glimpse into the thermochemistry happening inside the piston chamber.**

KEVIN CEDRONE: It's easy to think of these engines as mechanical engineering or physics, but there's actually a lot of chemistry going on. And so, what's interesting here is that, instead of doing the chemical reactions in a lab, on a stand, in a beaker, this is being done in real time, in an engine. And you can't take the same careful measurements to see what's going on with the chemistry that you can in that case, and so you've gotta use thermodynamics to back out what's going on inside the engine from what you can measure, the temperatures and the pressures, and those sorts of things, and so, getting a window into the chemistry is an interesting challenge and finding out what's going on from measuring around the problem instead of measuring in the problem is actually a challenge I like.

*[WRAP-UP]*

NICOLE LABBE: Using the energy from chemical reactions is something we've have been doing for thousands of years. But our understanding of where that energy is coming from and how it behaves is pretty new, relatively speaking. Thermodynamics as a field is only a couple hundred years old.

And in the last 200 years, we have used that knowledge to do some pretty cool stuff. I can't wait to see what we come up with next as we continue to explore the heat and the energy of chemical reactions.

*[END]*