**Chemistry: Challenges and Solutions**
**Unit 9: Equilibrium and Advanced Thermodynamics**
**Balance in Chemical Reactions**
Hosted by Wilton Virgo

*[Tease]*

**We often think of a chemical reaction as having a distinct beginning and end like a race. And there are many chemical reactions that behave this way. But most reactions never stop. Instead, they reach a steady state of constant motion – a state of chemical equilibrium.**

**Billions of equilibrium reactions occur in our bodies every second.**

DANIEL DESCHLER: That's fascinating, and that's what we do in medicine. We try to take this human being that's in this functioning equilibrium and realize when there's something eschew, how we can make it better.

**And over 100 years ago, the successful manipulation of an equilibrium reaction on the industrial scale would forever change the course of human history.**

THOMAS HAGER: This discovery is creating the food that is feeding almost half the people on earth. It's hard to imagine a technology that's more important than that.

**Saving lives and feeding the world. Just two of the many benefits gained by mastering the delicate and dynamic nature of chemical equilibrium.**

*[Title: Chemistry Unit 9: Equilibrium and Advanced Thermo Dynamics]*

**What can rust tell us about chemical reactions?**

WILTON VIRGO: Hi, I'm Wilton Virgo, a chemistry professor at Wellesley College.

What is rust? When steel, a mixture of iron and carbon, like the metal in this sculpture, meets water and oxygen, the iron in the steel reacts. This causes the iron to become a hydrated iron oxide, which we call rust. Most of us are familiar enough with rusting to understand that this is a chemical reaction that proceeds all on its own. Chemists refer to this type of reaction as spontaneous.

And there are many chemical reactions in the world that are spontaneous. When that's the case, the reaction in the opposite direction is not spontaneous. Let's look again at our example with iron.

To make steel, we need pure iron, or as close to pure iron as we can get. But because iron spontaneously reacts with oxygen, iron in its pure metallic form does not exist naturally on Earth.

As a matter of fact, most iron on the planet exists as iron oxides, which we call iron ore. So what do we need to do to get the iron and oxygen to separate? We need to get the reaction to go in the non-spontaneous direction, and this takes a lot of chemical work, because it is a reaction that does not really want to happen. And that, for the most part, is what's going on in a steel mill.

*[SEGMENT 1: Dynamic Equilibrium]*

WILTON VIRGO: Determining which way a chemical reaction will go is an important part of thermodynamics. However, this is not always a "one way or the other" determination. It's true that some reactions can only go in one direction, but many reactions proceed in both directions, and some of these will do both the forward and reverse reactions dynamically at the same time. We call these last ones equilibrium reactions.

To better understand what it means to be in chemical equilibrium, let's talk about what it doesn't mean. There are two big misconceptions about chemical equilibrium.

One is that once a chemical reaction reaches equilibrium the reaction has stopped. But this isn't true: an equilibrium reaction is a dynamic process where reactants are continuously turning into products and products are continuously turning back into reactants at the same time, and at the same rate.

A second misconception is that if a reaction is in chemical equilibrium there are equal parts reactants and products. Even though the word "equal" is part of equilibrium, this isn't true either. Once a reaction is at equilibrium, the concentrations of the products and reactants don't change, but their values don't have to match each other.

*[SEGMENT 2: The Equilibrium Constant]*

WILTON VIRGO: In some equilibrium reactions the concentrations of the reactants and to the concentrations of the products may be quite close. Like this – if you think of either side of this balance board as a representation of the concentrations of the products and reactants. In other reactions, the products may be favored, and in some, it goes the other way, towards the reactants.

The ratio of the concentrations of products to reactants in an equilibrium reaction provides what we call the equilibrium constant of a reaction, symbolized by the letter K.

**The value of K reveals which direction a reaction may favor. If K is close to one, then the concentrations of reactants and products are close to each other. So neither side of the reaction is really favored. However, if K is more than one, then there are more products, so the forward direction is more favorable, and if K is less than one, then there are more reactants and the reverse direction is favored.**

*[SEGMENT 3: DEMO – Le Chatelier's Principle]*

WILTON VIRGO: Equilibrium reactions have an amazing characteristic – they want to stay in equilibrium. When we disturb at equilibrium by applying a stress to the system, the system responds by changing its concentrations to shift to a new equilibrium position.

This phenomenon was discovered by French chemist Henri Louis Le Chatelier and is known as Le Chatelier's Principle.

Let's take a look at Le Chatelier's principle in action. Here I have two nearly colorless solutions. Over here, I've got iron (III) nitrate, which provides $Fe^{3+}$ ions. And here I have potassium thiocyanate, which provides thiocyanate ($SCN^-$) ions.

I'm going to mix these two together. So now we form iron thiocyanate, which has this nice deep red-orange color. Let's look at what happens when we disturb the equilibrium reaction.

In these three test tubes, I have the same solution that we just made. Next, I'm going to add more iron three ions to the solution. This will tip the equilibrium in favor of the reactants. So, according to Le Chatelier's Principle, what do you think will happen next?

We see as we add more iron (III) nitrate to the mixture, it turns a darker red color. We added more reactants, so the reaction responded by using the extra reactants to create more products. As Le Chatelier's principle tells us, the reaction tried to counter the change we imposed on the equilibrium reaction.

So how can both of these be at equilibrium if they are different colors?

Well, remember: K, the equilibrium constant always has the same value for a given reaction at a certain temperature. And in this reaction, K is 138 at 25 degrees Celsius. So any ratio of products and reactants that gets us to 138 will get us a happy reaction. This means that the concentrations of reactants and products can vary and we can still be at equilibrium.

Let's look at what happens when we affect equilibrium in a different way. I'm going to add a few drops of sodium hydroxide to the third test tube. We see the solution get a little bit cloudy. That's because a precipitate is forming inside the solution.

Sodium hydroxide reacts with the iron (III) ions to form iron hydroxide. So essentially, we are removing iron three ions from the solution and forming this precipitate. If I run this third solution through a centrifuge, it allows me to separate out the components so the precipitate settles down to the very bottom of the test tube. The solution is lighter in color. We tipped the reaction in favor of the products by removing some of the reactants, and the reaction shifts to the left in order to fill in that void.

Again, all three solutions look different in terms of their color, but they are all at an equilibrium state with the same value for the equilibrium constant K.

*[SEGMENT 4: Treating Poison]*

WILTON VIRGO: At the Norman Knight Hyperbaric Medicine Center at Massachusetts Eye and Ear Infirmary in Boston, Massachusetts, they are constantly dealing with two reactions that have very different equilibrium constants.

DANIEL DESCHLER: My name is Dan Deschler, and I direct the Hyperbaric Medicine Center here at the Massachusetts Eye and Ear Infirmary.

Hyperbaric oxygen therapy has many uses. And one of the most significant areas is for the management of carbon monoxide poisoning. And here it is quite helpful in reversing the immediate poisoning effects of carbon monoxide as well as preventing long-term neurologic or other effects of that poisoning.

Carbon monoxide is the byproduct of incomplete combustion. And so one of the groups of people who are most affected are firefighters because they will have the highest exposure to this toxin during fires. But firefighters aren't the only ones who are exposed to high levels of carbon monoxide. We can also have it in incomplete combustion of heaters in homes, or a car left on in a garage with a closed door. And so, if you look at national statistics, about 15,000 people per year will present to an emergency room to be treated for the effects of carbon monoxide poisoning. And of those, between four and 500 will die per year of that.

**Carbon Monoxide ties up our body's ability to perform the core function of delivering oxygen to its cells.**

**The air we breathe is about 21% oxygen, and the rest is mostly nitrogen. In our lungs, oxygen binds with a protein in our red blood cells called hemoglobin, to form oxyhemoglobin. This binding is a chemical equilibrium where neither the forward nor reverse direction is heavily favored. So in the lungs, where the concentration of oxygen is quite high, the reaction responds to create more products – the oxyhemoglobin.**

**The oxyhemoglobin then travels to different parts of the body where there is very little oxygen.  This causes the reaction to favor the reverse direction, releasing oxygen to the surrounding tissue.**

DANIEL DESCHLER:  The hemoglobin molecule came into existence because it does this role perfectly. It binds to oxygen at just the right level in the lungs to attract it over. And then, when the hemoglobin gets to the tissues that don't have a lot of oxygen, it readily gives up the oxygen molecule. So the balance is just perfect to do the task it needs to do, which is, take oxygen from the air and deliver it to the cells.

**Carbon monoxide also likes to react with hemoglobin to form carboxyhemoglobin. This is also a chemical equilibrium but one that is much more one-sided in the forward direction towards the products. This means that carbon monoxide has a much stronger attraction to hemoglobin than oxygen does, and so if we inhale even a very small amount it will quickly bind to the hemoglobin to try to reach equilibrium. And outside of the lungs, the hemoglobin is less likely to release any of the carbon monoxide because the reaction is happiest when there is a heavy concentration of the products.**

DANIEL DESCHLER: And that carbon monoxide molecule is 240 times more likely to bind to that hemoglobin molecule and then take off. And one of the tricky things about it is it changes the hemoglobin so it can't bind any of the oxygen. So off it goes with one carbon monoxide there, and then it comes back and it's still bound. And so it really impairs the body's ability to get oxygen to the heart, the brain, and critical tissues.

**The first step in treating someone who has been exposed to carbon monoxide is to get them away from the exposure.**

DANIEL DESCHLER: So now at least the body can work on trying to get rid of carbon monoxide through the lungs. Oxygen molecules can maybe bump it off and it gets breathed out. And then over time those molecules will leave the body completely.

But we may want that to go faster. So how can we make it go faster? Well, what we could have someone do is breath 100 percent oxygen. So now when that hemoglobin molecule comes around with its carbon monoxide bound to it, there are five times as many oxygen molecules that can try to bump it off. And that greatly improves the body's ability to get rid of carbon monoxide by about fourfold.

Then, can we do it even more?

And that's what a hyperbaric chamber does. We create a closed system so that we can pump more oxygen into that system. But, because it's closed and can't diffuse away, it's going to increase the pressure of that system.

So if you put someone in a hyperbaric medicine chamber, and go to three times the normal pressure, what that does is triple the amount of oxygen that someone is exposed to. And so now, when the hemoglobin molecule comes around, the oxygen molecules are in such high concentration they readily bump off the carbon monoxide.

**The oxygen and hemoglobin reaction is an important example of how different equilibrium reactions can have very different characteristics, and it is just one of millions of important equilibrium reactions which allow the human body to function on a daily basis.**

DANIEL DESCHLER: I think that one of the most fascinating things about these reactions that occur in the body is they are always in constant motion. There isn't just a molecule goes in one direction, goes there, then goes to the next place and it follows a direct line. There's billions and billions and billions of molecules, which are rolling back and forth in a constant, you know, ever-changing dance. And that's fascinating and that's what we do in medicine is we try to take this human being that's in this functioning equilibrium and realize that there's something eschew, how we can maybe make it better. And that's chemistry.

*[SEGMENT 5: DEMO – Pressure and Le Chatelier's]*

WILTON VIRGO: Changing the concentrations of the products or the reactants is not the only way we can put a stress on an equilibrium reaction. Let's take a look at the effect pressure changes have on equilibrium.

DANIEL ROSENBERG: What we have here in this syringe is a mixture of gases. One of these gases is nitrogen dioxide or NO2. It's a brown gas, and it's the gas that we see. The other gas is dinitrogen tetroxide, or N2O4. And that gas is also in there, but it's colorless, and we don't see it. And those two gases are in equilibrium, and that means the brown gas is turning into the colorless gas, and at the same time the colorless gas is turning into the brown gas. And that's happening all the time, very quickly, at equal rates. And the result is that it stays the same color. But we do have a way of changing that. When you make a change to an equilibrium, you push it out of balance, it will naturally find its way back into balance. And that is what we call Le Chatelier's Principle.

So one way we could disturb the equilibrium of the gas in this tube is by changing the pressure. And I can change the pressure by pressing in the plunger on this syringe. So when I compress it, it gets darker. But then it fades back towards the equilibrium color. When I release it, it gets lighter, and then fades darker towards the equilibrium color.

When we change conditions, so that we make more of one or the other, the reaction naturally goes back to its preferred state. So when we compress the gas it initially turns a very dark brown, we've concentrated the nitrogen dioxide by compressing it. But because of the equilibrium, very quickly those extra NO2s combine and form N2O4, which is colorless. So, the dark color fades out and it turns pretty much back into the same color that we see when it's not compressed. And then when we release it, there's only a little bit of the brown gas, so that fades, but there's lots of the colorless gas. And that colorless gas, in order to meet the conditions of equilibrium, breaks up and forms more of the brown gas.

And that is Le Chatelier's Principle.

WILTON VIRGO: Temperature also has an effect on equilibrium, but in a different way. When we change the temperature, we also change the equilibrium constant. We change K – so that when you change the temperature we bring the reaction to a new equilibrium state.

*[SEGMENT 6: DEMO – Temperature and Le Chatelier's]*

DANIEL ROSENBERG: Let's take a look at how temperature affects equilibrium.

What we have here are two tubes full of a mixture of gases. There's a brown gas, NO2, and a colorless gas, N2O4. And they're in equilibrium. But, we can change where that equilibrium point is by changing the temperature of the gas. And so, what happens when I put the room temperature tube into the boiling water bath?

Now it forms a dark brown mixture. So if we compare the hot gas mixture and the room temperature gas mixture, we can see that the hot gas mixture has more of the brown gas and less of the colorless. The room temperature mixture has more of the colorless gas and less of the brown, so it's a lighter color. They're both at equilibrium, but by changing the temperature we change the ratio that these two gases prefer to be in.

So what happens when we take the hot gas mixture and put it into an ice bath? Which way will it go? It looks like the gas mixture is starting to become lighter. At the temperature of ice water, we've got an equilibrium where there is more colorless gas than there is brown gas. In all three cases, there's an equilibrium – the reactions are moving forward and backward at the same rate. But how much of the brown gas and how much of the colorless gas changes depending on temperature.

So by changing the temperature, we change the equilibrium.

*[SEGMENT 7: The Haber Process]*

WILTON VIRGO: Le Chatelier's principle gives us the framework to understand how to shift an equilibrium reaction in our favor. And over 100 years ago, two chemists used that framework to develop a process that would change the path of human history.

**It all starts in 1898 in a small theatre in Bristol, England. William Crookes, the newly elected president of the British Association for the Advancement of Science delivers his inaugural address.**

THOMAS HAGER: Sir William Crookes was an unusual guy in many ways – he displayed his personality through his facial hair, he spoke quietly but he liked to shake things up. So he built his inaugural address, his first display as president, around the theme of imminent crisis. And he told his audience that the globe was about to undergo a period of mass starvation.

SAM KEAN: The basic problem was that we needed more fertilizers, and the basic point of fertilizers is to get nitrogen into the plants.

THOMAS HAGER: Nitrogen is essential for life. Every protein and every molecule of DNA has nitrogen in it.

SAM KEAN: And nitrogen is very abundant – four out of every five molecules you breathe are nitrogen, it's in the air all around you.

THOMAS HAGER: It is unusable because it exists in a form in which two nitrogen atoms are bonded to each other and frozen. That's a triple covalent bond, it's some of the strongest chemical bonding possible. The challenge for chemists was to break those two nitrogen atoms apart and combine them into another form. It was called "fixed nitrogen," and over millennia, millions of years, the Earth built a small, but very vital, store of fixed nitrogen, and the growing human population was using it so fast to grow crops that we were about to run out.

So, Crookes, in his speech, laid down a challenge: find a way to make synthetic fertilizer, or the entire globe is going to start going hungry.

SAM KEAN: This was really the biggest chemical prize out there at the time, and you knew that if you solved this, your name would basically be immortal. You would be one of the greatest chemists who ever lived.

THOMAS HAGER: That's where the world stood in 1905. And then came a brilliant but eccentric German chemist whose name was Fritz Haber. And he applied himself to the nitrogen problem from a different angle.

The trick that Haber discovered was that you could burn nitrogen apart in a little oven not with a flame, but just with heat. So he thought he could make a machine that could take nitrogen out of the air and combine it with hydrogen to make ammonia.

SAM KEAN: So the basic chemical equation to make ammonia is you have N2, you add three H2 molecules, and if you can get them to react together you can produce two molecules of ammonia, NH3.

RICHARD SCHROCK: NH3 can be decomposed, and that's the reverse reaction. So the challenge was to alter the equilibrium so that you get a significant amount of ammonia.

THOMAS HAGER: From 1905 to 1909, Haber and a very talented co-worker named Le Rossignol worked on putting hydrogen gas and nitrogen gas in a machine that was built to withstand temperatures and pressures that had never been harnessed before. And for the next four years, they made use of Le Chatelier's principle. And they fooled with the temperature, they fooled with the pressure, and they made the temperatures high enough to blow the nitrogen apart, but the temperature could be varied depending on the pressure. As you increase the pressure, you could also lower the temperature. That meant more ammonia would form, so they played with temperature and pressure. Then, they started finding ways to pull the ammonia out as soon as it was formed.

RICHARD SCHROCK: Pulling out ammonia was really a change in the concentration: if you remove ammonia, there's suddenly none there, essentially, so the equilibrium shifts and makes more. So that's the classic way to get a reaction to go to completion using

Le Chatelier's principle, is to remove one of the products.

THOMAS HAGER: Four years of work. Finally, in 1909, they were able to fire up a little tabletop machine, about the size of three desk lamps, ran their gases through it, and on the output side they got drops of ammonia. For hours on end – drop, drop, drop.

Haber found a way to answer Crookes' challenge. One of the chemical companies most interested in his work was BASF. The problem for BASF was how to take Haber's prototype and ramp it up to the size of a factory.

RICHARD SCHROCK: Scaling up was a dangerous, dangerous proposition, and it was unknown how you would do that.

THOMAS HAGER: The man they put in charge of that process was Carl Bosch. Carl Bosch was BASF's *wunderkind* chemist, he was a brilliant young man, and they faced terrific challenged. One after another, they knocked them down. They went from Haber's prototype, this little tabletop machine, to a factory that employed 10,000 workers within the space of five years. The original Haber-Bosch factory, which opened in 1913 in Germany, has now been replicated hundreds of times over. And now, half the nitrogen in your body came out of a Haber-Bosch factory. Haber-Bosch is responsible for keeping alive more than half the people on Earth. It's hard to image a technology that's more important than that.

*[WRAP-UP]*

WILTON VIRGO: The Haber-Bosch process marked a new era of chemical and industrial manufacturing where chemists started to manipulate and engineer equilibrium reactions to tip them in the direction that *we* want, in order to create the products that *we* need.

And that's what I absolutely love about chemistry. Because in chemistry, we are not only interested in how matter behaves, we use our knowledge to change that behavior for our *own* purposes.

And that's when the fun begins.

*[END]*